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REACTOR FUEL PROCESSING

A Quarterly Technical Progress Review

Prepared for DIVISION OF TECHNICAL INFORMATION, USAEC, by
STEPHEN LAWROSKI and ASSOCIATES, ARGONNE NATIONAL LABORATORY

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TECHNICAL PROGRESS REVIEWS

To meet the needs of industry for concise summaries of current atomic developments, the Atomic Energy Commission is publishing this series, Technical Progress Reviews. Issued quarterly, each of the reviews digests and evaluates the latest findings in a specific area of nuclear technology and science.

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Power Reactor Technology, formerly prepared and edited by W. H. Zinn and J. R. Dietrich, Nuclear Division, Combustion Engineering, Inc. (a new contractor will take over preparation of this journal beginning with Vol. 8, No. 4).

Reactor Fuel Processing, Stephen Lawroski and associates, Chemical Engineering Division, Argonne National Laboratory

Reactor Materials, R. W. Dayton, E. M. Simons, and associates, Battelle Memorial Institute

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REACTOR FUEL PROCESSING

A REVIEW OF RECENT DEVELOPMENTS

Prepared for DIVISION OF TECHNICAL INFORMATION, USAEC,
by STEPHEN LAWROSKI and ASSOCIATES,
ARGONNE NATIONAL LABORATORY

SUMMER 1965

VOLUME 8

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Foreword

This quarterly review of reactor fuel processing has been prepared at the request of the U. S. Atomic Energy Commission, Division of Technical Information. It is intended to assist those interested in keeping abreast of important developments in this field. In each Review it is planned to cover those particular subjects in which significant new results have been obtained. The Review does not purport to abstract all the literature published on this field during the quarter. Instead it is intended to bring each subject up to date from time to time as circumstances warrant.

Interpretation of results, where given, represents the opinion of the editors of the Review, who are personnel of the Argonne National Laboratory, Chemical Engineering and Idaho Divisions. Those taking part in the preparation of this issue are J. Barghusen, G. Bennett, L. Burris, Jr., P. Fineman, A. A. Jonke, G. Kesser, S. Lawroski, W. J. Mecham, D. Paige, J. Royal, J. Simmons, R. K. Steunenberg, C. E. Stevenson, and R. C. Vogel. The reader is urged to consult the original references for more complete information on the subject reported and for the interpretation of results by the original authors.

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Section

I

Reactor Fuel Processing

Commercial Aspects of Fuel Processing

Fuel-Processing Plans

Commercial Isotopes Plant at Hanford

The Atomic Energy Commission (AEC) has selected a joint proposal by Martin Marietta Co. and the United States Rubber Company as the basis for negotiation of a contract for commercial construction and operation of a facility to recover fission products at the Hanford Plant near Richland, Wash., and for operating its chemical processing complex. This is the third contractor selection in the transfer of work from General Electric Company (GE) to other firms. The transfer program was mutually agreed to by the AEC and GE in January 1964. Battelle Memorial Institute, Columbus, Ohio, took over operation of Hanford Laboratories (renamed the Pacific Northwest Laboratory) at the first of this year. The United States Testing Co., Inc., Hoboken, N. J., assumed responsibility for radiation-protection services at the same time.[1]

It is reported that the joint venture of Martin Marietta–United States Rubber on the Hanford fission-products plant will not seek financial aid from the AEC. The estimated cost of construction is $8 million. Operations are scheduled to begin about mid-1968. The plant will be built on land leased from the AEC.[2]

Qualified Organizations Invited To Participate in NRTS

Proposals are being sought by the AEC[3] from qualified organizations interested in conducting certain programs at the National Reactor Testing Station (NRTS) near Idaho Falls, which are now carried out by Phillips Petroleum Company under a contract expiring in February 1966.

The move to offer other organizations an opportunity to perform work at NRTS is a further implementation of AEC policy announced in May 1963, wherein it was stated that added opportunity to compete for supplying services to the AEC would be offered to organizations which have made significant private investment in the field of atomic power and which do not have a major operating contract with the AEC.

Portions of the NRTS operations which will be transferred to a new contractor include the chemical processing plant, three test reactors, and central service functions such as shops, library, utilities, transportation, and cafeterias.

The reactor safety program to remain with Phillips includes the Special Power Excursion Reactor Test (SPERT), the Power-Burst Facility (PBF), and the Safety Test Engineering Program (STEP) which includes the Loss of Flow Test (LOFT).

Representatives of Phillips and the AEC are meeting to work out details of the transition. No reduction in program or in overall employment levels is expected as a result of the change.[3]

AEC Encourages Growth of Commercial Plutonium-Processing Capability

A review by the AEC of its requirements for plutonium fuels and the availability of commercial capability to perform plutonium-processing services has shown that within a few years plutonium-fuel requirements will outgrow the present processing capacity. The AEC, through its Division of Industrial Participation, is taking steps to give further encouragement to the growth of a competitive commercial operation in the area of plutonium-fuel processing, which includes conversion to oxide,

carbide, or metal fuel materials and the fabrication into reactor fuel elements.[4]

Information Sought by AEC on Processing Plans of U. S. Firms

The AEC is seeking information from selected private companies concerning their intentions to provide chemical processing service for the recovery of materials from fuel elements that have been irradiated in nuclear reactors.[5]

This information is to be used to guide AEC programs in support of the long-term minimization of fuel-cycle costs to the power-reactor industry. One aspect of this interest concerns the high transportation costs for the heavy shielding casks for shipping spent fuels from reactors to processing plants. Since one commercial processing plant is located in the East, namely, Nuclear Fuel Services, Inc., in the state of New York, new plants may advantageously be located in the West. The AEC has invited industrial firms to consider location at the Hanford site, near Richland, Wash.

One aspect of AEC interest in fuel processing concerns the possibility of a guaranteed base load for commercial plants. Also involved is the extent of dependence upon research and development in the AEC programs. Projected plant loads and times at which such plants would be operating enter into future prospects of the economic development of nuclear power.[5]

U. K. Atomic Energy Authority Prepares for Commercial Operations

It has been reported that the British government announced that most of the fuel-element-production activities of the U. K. Atomic Energy Authority (UKAEA) will be carried on as a commercial venture on a wholly separate financial basis from the rest of the UKAEA. The purpose of the new arrangement is to "provide a suitable financial basis for the Authority's fuel element business," which is based at the Springfields fabrication plant.[6] The Capenhurst gaseous diffusion plant and the Windscale chemical processing operation will not be affected by the present change but are to be considered for inclusion in the commercial venture later.[7] The Dounreay chemical processing plant for highly enriched fuels was not cited in the present proposal.

The new commercial complex will include the production reactors at Calder Hall and Chapelcross, which are now operated primarily to generate electricity, and the Amersham radiochemical operation, which is a major facility for the preparation of radioisotopes for distribution.[6]

Utilization of Plutonium in the United Kingdom

A review has been published of UKAEA studies on the utilization of plutonium in the United Kingdom. The reactor-physics problems in both thermal and fast reactors were compared, and the value of plutonium to individual reactor systems was assessed. On the basis of comparative value to ^{235}U fuel, the estimated plutonium-fuel values (based on 1 pound sterling equaling $2.80) ranged from $8.4 per gram of fissile plutonium (a lower limit for thermal-reactor use) to $19.6 per gram of fissile plutonium (an upper limit for fast reactor use). An alternative evaluation method is also proposed, wherein plutonium is considered as an intermediate product in an integrated system of plutonium-producing and plutonium-burning reactors. In this approach there is no need to assign a market value to plutonium since the aim here is to provide a minimum overall generating cost.[8]

The development of plutonium-fueled reactors is given an important place in the UKAEA experimental programs. On the production side, it is estimated that about 20 metric tons of plutonium will have been produced in the U. K. thermal power reactors by 1976, assuming the installation of 5000 Mw(e) of Advanced Gas-Cooled Reactors (AGR), in addition to the present program of 5000-Mw(e) Magnox reactors. The assessments of this study indicate that plutonium-fueled fast reactors have the potential of producing power more cheaply than any other reactor system so far envisaged.[8]

Economics of the Fuel Cycle

AEC Purchase Prices for Plutonium and Uranium-233

The AEC has established new guaranteed purchase prices[9] for privately owned plutonium

and for uranium enriched in isotope ^{233}U. The establishment of these prices is one of the actions which has been taken by the AEC to implement the Private Ownership of Special Materials Act passed by the 88th Congress in August 1964. The prices pertain only to material produced in a nuclear reactor licensed under Section 104 of the Atomic Energy Act and produced "through the use of special nuclear material which was leased or sold by the Commission pursuant to Section 53." Further details of the specifications are given in the *Federal Register* for Mar. 25, 1965. The guaranteed prices are:[9]

> For plutonium in the forms of nitrate, dioxide, or metal (each meeting AEC specifications), $10/g of the contained isotopes plutonium-239 and plutonium-241.
>
> For uranium enriched in uranium-233 in the forms of nitrate, dioxide, or metal (each meeting AEC specifications), $14/g of the contained isotope uranium-233, subject to adjustment for the presence of other uranium isotopes and deductions for handling costs.

These prices are the ones expected in the light of previously published AEC studies of the economic fuel values for fissionable materials. The significance of the price regulations on private nuclear firms is discussed in Ref. 10.

Cost Study of Carbide-Fuel Processing

Atomics International has issued a report on the comparative fuel-cycle evaluation of the CARBOX process (a low-decontamination pyroprocessing method) and of aqueous processing for carbide fuel in a thermal reactor.[11] This report is reviewed in Sec. III.

Shipping of Spent Nuclear Fuel

Evaluation and approval of casks for shipping of spent fuel in the United States are carried out by the AEC licensing staff, applying the proposed regulation 10 CFR 72. Reference 12 contains a list of 24 designs approved for specific fuels as of Feb. 1, 1965. The list identifies the size and other information on the casks.

The commercial shipment of spent nuclear fuel from the Dresden, Ill., plant of the Commonwealth Edison Company to the Nuclear Fuel Services processing plant in upstate New York is under negotiation with railroad companies. Negotiations have reportedly been concerned with special contracts to define liability. Under the conditions that the single flatcar carrying the loaded shipping cask be treated as a separate train, a proposed charge rate is $7.30 per mile plus $1.40 per 100 lb for the loaded cask. For the return trips, with the car carrying the empty cask, the charge proposed[13] is $1.31 per 100 lb.

The following papers on shipping of spent nuclear fuel were presented at the Fifty-Seventh Annual Meeting of the American Institute of Chemical Engineers at Boston, Mass., December 6–10, 1964:

L. L. Zahn, Jr., and R. L. Junkins, Safety Aspects of Transport of Radioactive Materials
R. Salmon, Economics of Irradiated Fuel Shipments
R. W. Peterson, Design of Containers
H. G. Clarke, Jr., Impact Resistance of Casks
A. E. Aikens, Jr., Practices and Procedures for Licensing
G. J. Appleton and J. Servant, International Packaging Standards
J. C. Glynn, Heat Removal from Casks
K. W. Haff, Radioisotope Shipping Container Development

These papers are to be published in *Chemical Engineering Progress, Symposium Series*, No. 56, Vol. 61 (1965), and will be considered for more detailed review.

AEC-Owned Patents Made Available for Licensing

The AEC has announced the titles and published abstracts of AEC-owned British,[14] French,[15] and German[16] patents for which it will grant licenses for royalties. From the total of 181 patents of this announcement, those in Table I-1 are the most pertinent to reactor fuel processing. (W. J. Mecham and A. A. Jonke)

References

1. Joint Proposal Selected as Basis for Negotiation on Hanford Fission Products Plant and Chemical Processing Work, AEC Press Release H-31, Feb. 9, 1965.
2. *Nucl. Ind.*, 12(2): 11 (February 1965).
3. AEC To Offer Other Organizations Opportunity To Perform Contract Work at NRTS, AEC Press Release H-29, Feb. 5, 1965.

Table I-1 AEC-OWNED PATENTS PERTINENT TO REACTOR FUEL PROCESSING

Patent No.	Issuance date	Patent title
		British Patents[14]
945,899	June 23, 1961	Separation of Uranium and Plutonium Oxides
946,513	Mar. 29, 1962	Preparation of Spherical Uranium Dioxide Particles
952,826	June 4, 1962	Separation of Uranium, Plutonium and Fission Products from Neutron-Bombarded Uranium
953,977	Mar. 29, 1962	Method for Preparing UO_2 Compacts
955,327	June 26, 1962	Dissolution of Uranium Fuels
957,354	Feb. 6, 1962	Ceramic Coated Fuel Particles
963,613	July 2, 1962	Precipitation of Zirconium and Fluoride Ions from Solutions
964,620	Sept. 17, 1962	A Process of Dissolving Fuel Elements of Nuclear Reactors
966,004	May 3, 1963	Method of Dissolving Plutonium
967,568	July 30, 1962	Fluorination of Oxidic Nuclear Fuel
970,627	May 28, 1962	Production of Uranium Monocarbide
970,849	Sept. 16, 1963	Plutonium Oxide Spheres and Method of Making
970,850	Sept. 16, 1963	Plutonium Recovery from Neutron-Bombarded Uranium Fuel
972,661	Apr. 16, 1963	Insolubilization of Fission Products
972,663	Apr. 18, 1963	Plutonium Recovery from Nuclear Fuel
977,510	Jan. 28, 1963	Immiscible Liquids Separator
979,324	July 9, 1962	Actinide Carbide Product and Method of Making
979,747	Sept. 11, 1963	Cladding of Nuclear Fuel Elements
979,884	Jan. 14, 1963	Process for Separation and Recovery of Volatile Fluoride Impurities from Uranium Hexafluoride
981,360	May 3, 1963	Separation of an Actinide Metal from an Alloy
981,532	Jan. 15, 1962	Dissolution of Uranium-Molybdenum Reactor Fuel Elements
981,784	Oct. 12, 1962	Liquid Phase Sintering of Metallic Carbides
		French Patents[15]
1,347,928	Nov. 30, 1962	Liquid Phase Sintering of Metallic Carbides
1,350,444	Mar. 13, 1963	Immiscible Liquids Separator
1,353,220	Mar. 12, 1963	Process for Separation and Recovery of Volatile Fluoride Impurities from Uranium Hexafluoride Containing the Same
1,358,227	June 4, 1963	Separation of an Actinide Metal from an Alloy
1,359,533	June 4, 1963	Nuclear Reactor Fueled with Suspended Particulate
1,362,715	May 7, 1963	Insolubilization of Fission Products
1,362,859	July 3, 1963	Process for Preparation of Uranium Metal
1,362,865	July 4, 1963	Plutonium Recovery from Nuclear Fuel
1,362,866	July 4, 1963	Method of Dissolving Plutonium
1,363,607	July 9, 1963	Regeneration of Hydrocarbon Solutions of Trialkyl Phosphate Used in Processing of Nuclear Fuel
1,369,638	Sept. 12, 1963	Preparation of Uranium Monosulfide
1,370,413	Oct. 2, 1963	Plutonium Recovery from Neutron-Bombarded Uranium Fuel

Patent No.	Issuance date	Patent title
		French Patents[15] (Continued)
1,370,989	Sept. 23, 1963	Cladding of Nuclear Fuel Elements
1,374,708	Nov. 8, 1963	Sintering Ceramic Shapes
1,376,103	Nov. 26, 1963	Solvent Extraction Apparatus
1,378,956	Sept. 30, 1963	Plutonium Oxide Spheres and Method of Making
1,384,543	Mar. 10, 1964	Uranium Recovery from Ore Concentrates
1,387,779	Apr. 10, 1964	Plutonium Separation from Uranium and Lanthanides by Precipitation from Molten Chloride Solutions
1,389,328	Apr. 15, 1964	Method for Preparation of Spherical Thorium Dicarbide and Thorium-Uranium Dicarbide Particles
		German Patents[16]
1,152,096	Apr. 7, 1960	Fluidized Solids Process and Recovery of Uranium from Zirconium-Type Fuel Elements
1,159,919	Apr. 29, 1961	Improved Stripping of Uranium from Organic Extractants
1,159,920	June 28, 1961	Uranium Separation Process
1,159,921	Aug. 18, 1962	Precipitation of Zirconium and Fluoride Ions from Solutions
1,160,647	June 13, 1959	Regeneration of Reactor Fuel Elements
1,161,545	July 20, 1961	Separation of Uranium and Plutonium Oxides
1,162,816	Oct. 4, 1961	Low Temperature Process for the Removal and Recovery of Chlorides and Nitrates from Aqueous Nitrate Solutions
1,165,873	Apr. 18, 1962	Processing of Uranium-Metal-Containing Fuel Elements
1,170,387	Sept. 25, 1962	A Process of Dissolving Fuel Elements of Nuclear Reactors
1,170,918	May 5, 1961	Improved Solvent Extraction Process for the Separation of Uranium and Thorium from Protactinium and Fission Products
1,170,919	Nov. 4, 1960	Method of Reprocessing UO_2 Reactor Fuel
1,171,409	Aug. 9, 1962	Fluorination of Oxidic Nuclear Fuel
1,173,885	July 12, 1961	Preparation of UO_2 for Nuclear Reactor Fuel Pellets
1,176,112	Nov. 24, 1961	Method for Separating Transplutonium Elements from Rare Earth Fission Products
1,178,047	May 29, 1962	Production of Uranium Monocarbide
1,178,216	July 14, 1962	Separation of Uranium, Plutonium and Fission Products from Neutron-Bombarded Plutonium
1,181,190	Mar. 31, 1962	Dissolution of Uranium-Molybdenum Reactor Fuel Elements
1,181,830	Mar. 17, 1962	Ceramic Coated Fuel Particles
1,182,838	June 21, 1963	Separation of an Actinide Metal from an Alloy
1,183,893	Sept. 28, 1963	Preparation of Uranium Monosulfide
1,184,092	Feb. 13, 1964	Uranium Recovery from Ore Concentrates

4. AEC Encourages Growth of Commercial Plutonium Capability, AEC Press Release H-63, Mar. 19, 1965.
5. AEC Solicits Information Concerning Industry Plans To Provide Chemical Processing Services, AEC Press Release H-57, Mar. 10, 1965.
6. *Nucl. Ind.*, 12(2): 18-19 (February 1965).
7. *Nucleonics Week*, 6(7): 5 (Feb. 18, 1965).
8. H. Kronberger and N. L. Franklin, Utilization of Plutonium in the United Kingdom, *J. Brit. Nucl. Energy Soc.*, 4(1): 37-44 (January 1965).
9. AEC Establishes New Purchase Prices for Plutonium and Uranium-233, AEC Press Release H-65, Mar. 25, 1965.
10. *Nucl. Ind.*, 12(2): 21-25 (February 1965).
11. K. L. Mattern and L. J. Colby, Jr., Comparative Fuel Cycle Evaluations, Low Decontamination Pyroprocessing and Aqueous Reprocessing. Part II. UC Fuel in a Thermal Reactor, USAEC Report NAA-SR-9335, Atomics International, Feb. 15, 1965.
12. *Nucl. Ind.*, 12(2): 26-27 (February 1965).
13. *Nucl. Ind.*, 12(3): 36 (March 1965).
14. 68 Commission-Owned British Patents Made Available for Licensed Use, AEC Press Release IN-556, Feb. 16, 1965.
15. 60 Commission-Owned French Patents Made Available for Licensed Use, AEC Press Release IN-563, Mar. 4, 1965.
16. 53 Commission-Owned German Patents Made Available for Licensed Use, AEC Press Release IN-573, Mar. 31, 1965.

Section

II

Reactor Fuel Processing

Research and Development on Aqueous Processing

Current interest in applying fluoride-volatility- and pyrochemical-process methods to the recovery of reactor fuels has resulted in lessening the scope of development work on aqueous processes. However, efforts are continuing on developing new dissolution techniques and on broadening solvent-extraction-process applications.

Preparation of Fuel for Recovery

There appears to have been no recent reported work of significance on mechanical fuel-preparation methods. The NH_4F dissolution of zirconium-uranium alloys and of Zircaloy cladding is reviewed, and the effect of irradiation on HNO_3 dissolution of ThO_2 particles is noted. Recent work on processing carbide fuels includes hot disintegration in acid, slurry extraction, and composition of gases from acid hydrolysis.

Decladding with Ammonium Fluoride

Development of an NH_4F decladding–HNO_3 dissolution procedure for Zircaloy-clad PuO_2-UO_2 fuel elements for the Plutonium Recycle Test Reactor (PRTR) was reported in the Fall 1964 issue of *Reactor Fuel Processing*.[1] This process[2] has recently been applied satisfactorily to short pieces of fuels irradiated to 2000 and 5000 Mwd/ton. Decladding was carried out in $5.7M$ NH_4F–$0.055M$ NH_4NO_3 to produce a solution containing $0.6M$ zirconium. The insoluble UF_4 formed in decladding was sufficient to provide a concentration of $0.15M$ fluoride in the $15.5M$ HNO_3 used for core dissolution and thus to ensure dissolution of PuO_2 in the core.

Dissolution of Zirconium-Uranium Alloys in Ammonium Fluoride

Zirconium-uranium alloys containing up to 8% uranium can be dissolved in about $6M$ NH_4F solutions with the addition of minor amounts of H_2O_2 to solubilize the uranium by its conversion to the hexavalent state. Peroxide also dissolves any tin present. If $0.6M$ to $1.0M$ NH_4NO_3 is also present, generation of hydrogen is markedly suppressed, and a less hazardous off-gas is produced. In both cases the off-gas contains considerable amounts of NH_3. If NH_4NO_3 is not used, the dissolver product can simply be diluted with water to permit solvent extraction of the uranium, but a stronger complexing agent than tributyl phosphate (TBP) must be used [di-2-ethylhexyl phosphoric acid (D2EHPA) and diamylamyl phosphonate in a hydrocarbon diluent, for example]. If the dissolver product contains NH_4NO_3, it is diluted with about two-thirds its volume of $1.8M$ HNO_3–$1.8M$ $Al(NO_3)_3$ to produce a feed solution suitable for TBP extraction. In both cases, dilution must be carefully controlled to provide proper ratios of uncomplexed fluoride to zirconium so that solutions will be adequately stable for processing and storing. Flow sheets for both these processes were presented in the July 1962 and January 1963 issues of *Reactor Fuel Processing*.[3,4]

Kitts[5] has recently summarized work at Oak Ridge National Laboratory (ORNL) on pilot-plant zirconium-alloy dissolution studies using NH_4F solutions and has made a comparison of the two process modifications. The studies were conducted both batchwise and continuously in 6-in.-diameter columns using alloys containing 1 to 8% uranium. In batch operations, H_2O_2 addition rates (as a 3 to 10% solution) of about 10^{-5} mole/(min)(cm^2) of initial fuel-alloy surface were sufficient to prevent

U(IV) precipitation when alloys containing up to 8% uranium were being dissolved. It was necessary to continue the addition of peroxide as long as zirconium was dissolving in order to prevent reduction of U(VI). For continuous operation the 6.6*M* NH_4F–0.6*M* or 1.0*M* NH_4NO_3 feed solution also contained 0.1*M* H_2O_2.

The gaseous reaction products with excess NH_4NO_3 amounted to 5 moles of NH_3 and less than 0.1 mole of hydrogen per mole of zirconium dissolved, along with traces of oxygen. After a scrubbing step with dilute HNO_3, the remaining gas was a flammable O_2-H_2 mixture that was readily diluted with air. In the absence of NH_4NO_3, the gaseous products were 4 moles of NH_3 and 2 moles of H_2 per mole of zirconium dissolved, again with traces of oxygen present. After the HNO_3 scrubbing step, the residual gas was rich in hydrogen and was above the flammability limit. Dissolution rates ranged from 2 to 20 mg/(min)(cm^2) in boiling dissolver solution, but it was found that the surface condition (presence of oxide films) and the free fluoride concentration strongly influenced the rates observed. For material typically in the form of plates having a thickness of about $\frac{1}{8}$ in., complete dissolution required 2 to 5 hr. If the ratio of free fluoride to uranium [calculated as: (moles of F–6 times moles of Zr)/moles of U] dropped below about 100, the appearance of a precipitate of UF_4 was likely to be noted.

Dissolver solutions produced were about 1*M* zirconium; these solutions required dilution before cooling to 0.3*M* to 0.6*M* zirconium with water or HNO_3-$Al(NO_3)_3$ to produce stable solvent-extraction feed solutions.

Extensive corrosion tests were made at 50°C with types 304L and 347 stainless steels, Carpenter-20SCb alloy, and a low-carbon nickel alloy in solutions representative of a variety of the process conditions, as well as testing these alloys in the form of coupons suspended in the pilot-plant dissolver. All four of the materials appeared potentially satisfactory for the process; maximum initial corrosion rates of 1.2 mils/month were observed, and the rates generally decreased to values of the order of 0.3 to 0.6 mil/month.

Dissolution of Mixed Thorium and Uranium Oxides

At Oak Ridge a sol-gel process has been developed for the preparation of small, dense ThO_2 particles that are very suitable for reactor fuel preparation. In this process,[6] ThO_2 particles, made by steam denitration followed by calcination (at 700°C), are converted to a sol with water. The sol is carefully evaporated to a gel, from which ThO_2 particles having 99% of the theoretical density are produced by calcination at up to 1150°C. An intimate mixture containing up to 10% UO_2 can be produced by adding UO_3 or $UO_2(NO_3)_2$ to the ThO_2 sol.

Methods for the dissolution of sol-gel-produced ThO_2-UO_2 were discussed in the Winter 1964–1965 issue of *Reactor Fuel Processing*.[7] Goode and Flanary[8] have noted that irradiation in the range 3000 to 90,000 Mwd/metric ton results in somewhat increased rates of dissolution in 13*M* HNO_3 containing 0.04*M* NaF and 0.04*M* $Al(NO_3)_3$ for sol-gel-derived ThO_2-UO_2, as well as for similar oxide mixtures made by pelletizing or arc fusing. Up to 95% of the irradiated oxides dissolved in 8 hr, as compared with 70 to 73% of the unirradiated oxides which dissolved in 7 hr. A cyclic dissolution procedure in which about three-fourths of the total material present was dissolved in each 5-hr period, followed by the addition of fresh reagent to the residue, was also found to be quite effective. Including several "heel" dissolutions, total recovery after 11 cycles was greater than 99.8%. The losses of thorium and uranium to the 6*M* H_2SO_4 solution used for decladding stainless-steel-clad specimens of oxides were as high as 0.33% of the oxide present.

Processing of Carbide Fuels

Work at the Idaho Chemical Processing Plant (ICPP) on means for preparing graphite–uranium carbide fuels, such as those used in the Rover-rocket-program reactors, for aqueous processing was described in the Winter 1964–1965 issue of *Reactor Fuel Processing*.[7] In continuation of this work, two modified techniques show some promise.[9] The first method involves hot disintegration with concentrated H_2SO_4-HNO_3 mixtures. Disintegration-leaching studies were conducted with a 75 vol.% H_2SO_4–25 vol.% HNO_3 mixture at 84 to 152°C, using fuel material that had undergone a 10-min exposure to hot H_2 at expected reactor temperatures. About 99% of the uranium was dissolved by 7-hr treatments at 118 and 152°C. It was also shown that uranium could be satisfactorily extracted from a graphite slurry pre-

pared from an acidic uranyl nitrate solution; this indicated that a solids-separation step might not be necessary for disintegration-leaching processes. Such a slurry, containing 30 g of graphite per liter in 0.03*M* UO_2^{2+} and 8*M* HNO_3, was effectively treated with 10% TBP in a hydrocarbon diluent in a 1½-in.-diameter pulse column, provided 200 ppm gelatin was added to the feed to prevent accumulation of solids at the interfaces.

Extensive studies of the composition of gases obtained by hydrolyzing uranium carbides have been made at Oak Ridge.[10] With water, H_2 and CH_4 were the principal products. Ferris and Bradley[11] now report that, by treatment with 2*M* to 16*M* HNO_3, the gases produced at 90°C consisted mainly of NO, NO_2, and CO_2 and that CO, H_2, and gaseous hydrocarbons were absent. Although material balances were poor, roughly one-half of the carbon present appeared in the gas phase, and similar amounts were found in water-soluble form. The carbides tested varied from UC to $UC_{1.85}$. Peculiarly, dilute HNO_3 (0.01*M* to 0.5*M*) appeared to passivate the carbides, and no reaction occurred.

Solvent-Extraction Processes

Purex-Process Performance for Short Contact Time

Typical packed or pulsed-plate columns, or mixer-settlers, now used to effect contact between aqueous and organic phases in solvent-extraction processes, are limited in their performance by the time and space required to effect both contact and adequate phase separation. For processes requiring stream flow rates of the order of gallons per minute, geometrically safe designs for processing fissionable materials are difficult or impractical. Since chemical and radiation deterioration of solvents and other reagents is essentially proportional to contact time, it is obviously desirable to minimize this parameter. It is well recognized that process flexibility could be improved if compact high-performance contactors, effectively operable with short contact times, were available. The development of several types of such contactors has been discussed previously. In Ref. 12 one group of British workers describes high-efficiency pulsed columns, and another, the safe-by-shape mixer-settlers. At Oak Ridge, development has been in the direction of stacked hydroclones.[13] At Savannah River[14] a centrifugal contactor has been developed.

Although short-contact-time equipment was developed, it remained to be demonstrated that the decontamination performance of the solvent-extraction process would not be limited by contact time. Schlea et al.[15] have confirmed the feasibility of using, for the Purex process, a contactor that allows the organic phase only a 4-sec contact time for each extraction stage.

The process tests were carried out in three 16-stage miniature centrifugal contactors, described in the January 1963 issue of *Reactor Fuel Processing*,[16] using impeller speeds of 4000 rpm and bowl speeds of 7000 rpm. Only a first-cycle partition-decontamination process was tested, using a relatively standard flow sheet for irradiated natural uranium [a solvent composed of 30% TBP in a paraffinic diluent, a 1.2*M* to 1.6*M* $UO_2(NO_3)_2$–1.0*M* to 1.4*M* HNO_3 feed, and a 3*M* HNO_3 scrub]. Both ferrous sulfamate and hydrazine-stabilized uranous nitrate were tested as reducing agents for plutonium. Twelve tests were conducted at varying feed-activity levels, extraction-contactor temperatures, and hours of solvent exposure at typical process radiation levels.

With normal solvent saturation in the extraction section (1A bank), gamma decontamination factors for both uranium and plutonium exceeded 10^4, and excellent separation of the two products was achieved. It was necessary to operate the first cycle at 55 to 65°C to secure good decontamination from ruthenium ($>10^4$) since decontamination at 35 to 40°C was only effected by a factor of about 600. Because of the short contact time in the partitioning unit (1B bank), it was also necessary to remove excess HNO_2 in the feed by heating in order to avoid excess losses (1 to 4%) of plutonium to the uranium-product stream. A plutonium concentration profile of the 1B bank showed that, without heating, Pu(IV) was not reduced to Pu(III) near the center of the bank because these stages were required to destroy the nitrite, and insufficient stages then remained to reduce plutonium completely. When the feed was heated during feed preparation, partitioning was satisfactory and less than 0.1% plutonium was lost. Both Fe^{2+} and U(IV) were found to be effective reducing agents for Pu(IV).

Consequently it appears that, for TBP processes at least, short contact times should result in adequate process performance, and this should permit operation upon highly irradiated fuels without serious solvent deterioration. (C. E. Stevenson)

Plant and Equipment Design and Operation

Radiation Resistance and Decontamination of Protective Coatings

In aqueous-processing-plant design, a protective coating that will withstand radiation and permit easy decontamination is very desirable for coating cell walls, equipment supports, etc. West and Watson[17] present some recent data on such coatings.

Although the tests performed do not lead to a comprehensive comparison of all materials, the results indicate that a very wide choice of materials is available for various conditions. Twelve manufacturers submitted samples, 57 of which could be exposed to radiation under deionized water and 62 of which could be exposed to radiation in air. In the radiation tests the coatings were applied to 2- by 6-in. 16-gauge steel and 2- by 2- by 6-in. concrete panels. The specimens were exposed to radiation from a 1.33-Mev ^{60}Co gamma source that produced an intensity of 0.9 to 2.08×10^6 r/hr. In the decontamination tests a portion of the sample was contaminated with a 0.1-ml solution of mixed fission products (Ce-^{144}Pr, Zr-^{95}Nb, and ^{106}Ru) at 0.86 to 3.0 r/hr. The solution was allowed to dry on the sample. After the activity was read with a hand-held radiation-monitoring instrument, the samples were rinsed with cold water for 2 min. The specimens were dried again; then another reading was taken, and the ratio of the activities was computed to give values of the water decontamination factor. The final decontamination was performed by submerging each sample in a solution of $3M$ HNO_3 at room temperature and then by scrubbing the samples with 25 forward and 25 backstrokes using a medium-hard brush and moderate pressure. A 1-min rinse in cold water and drying in air, followed by a third activity measurement, completed the procedure. The ratio of the original activity value to the value of the third measurement was recorded as the total decontamination factor. The coatings were further evaluated by visual observation and physical comparison.

West and Watson[17] present detailed tables that give all the data obtained on the many coatings tested; these tables are valuable references. They also make some specific recommendations for various postulated conditions. In general, epoxy coatings were more resistant to gamma radiation than other organics, and vinyls were easier to decontaminate. Some of the epoxies were serviceable after an exposure of 1×10^{10} r in air. The vinyls were resistant up to 6×10^9 r in air. In water these values were reduced by approximately a factor of 10. The total decontamination factors for some of the vinyls were reported as 5×10^3, and for epoxies, 500 to 1000. From the data presented it would seem desirable to use epoxies where high radiation is involved and vinyls in moderate radiation areas, especially where decontamination would be necessary. Of course, cost, chemical resistance, and other factors may affect the choice of coatings.

Reference 17, as well as some of the other references listed, should prove to be a valuable tool in the design of radiochemical plants and hot cells.

Pulse-Column Study

Extensive engineering studies are reported by Ryon and Lowrie[18] in which sieve-plate pulsed columns, using a di-*sec*-butylphenyl phosphonate (D-*s*-BPP) solvent-extraction process, are evaluated for the separation of uranium from thorium. The studies were undertaken to provide design data for an extraction system to purify ^{233}U to be used as feed for the sol-gel process. Other studies at Oak Ridge[19] have indicated that the D-*s*-BPP solvent would show a separation factor 10 times greater for uranium from thorium than the factor obtained with TBP. Also, the radiation stability of D-*s*-BPP, its chemical stability, and its effectiveness in separating uranium from fission products are all better than those of TBP. Figure II-1 shows two flow sheets utilizing D-*s*-BPP.

The essential equipment used consisted of standard test columns composed of 2-ft sections of precision-bore 2-in. glass pipe (Fig. II-2). The sieve plates used had 0.125-in.-diameter holes, 23% free area, and were spaced

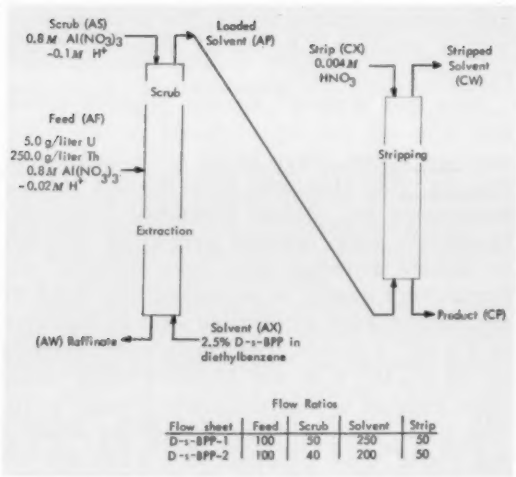

Fig. II-1 Flow sheets for D-s-BPP process.[18]

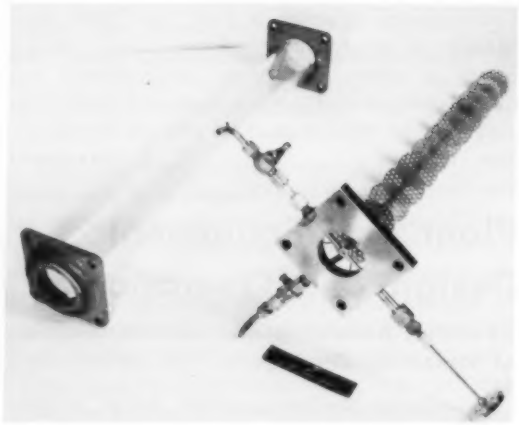

Fig. II-2 Standard column section.[18]

Table II-1 FLOW CAPACITY FOR SIEVE-PLATE PULSED COLUMNS[18]

Pulse frequency, cpm	Compound extraction-scrub column		Stripping column	
	Flow capacity, gal/(sq ft)(hr)	Dispersed-phase holdup at 90% flooding, %	Flow capacity, gal/(sq ft)(hr)	Dispersed-phase holdup at 90% flooding, %
		Flow Sheet 1		
35	1340	33	730	31
50	910	23	490	23
70	700	25	380	25
90	490	29		
		Flow Sheet 2		
35			860	33
50	990	28	530	24
70			400	25

Table II-2 SUMMARY OF COLUMN-EFFICIENCY DATA FOR D-*s*-BPP FLOW SHEETS OPERATED AT ABOUT 80% OF FLOODING[18]

Experiment No.	Flow sheet No.	Uranium					Thorium scrubbing	
		Extraction			Stripping			
		Pulse freq., cpm	HETS, ft	HTU, ft	Pulse freq., cpm	HETS, ft	Pulse freq., cpm	HETS, ft
26-230	1	50	4.0	0.98	35	12.0	50	4.6
26-222	1	70	2.1	0.62	50	6.7	70	4.1
27-320	1				70	4.2		
27-301	2	50	4.1	1.14	35	12.0	50	6.2
30-370	2						50	13.0*

*Column was operated with the solvent phase continuous.

2 in. apart. The extraction-scrub column was 24 ft high; the top 8 ft was used as a scrub section for flow sheet 1, and the top 12 ft, for flow sheet 2. Stripping tests were made in a 12-ft column. Both columns were operated with the aqueous phase continuous and a 1-in. pulse amplitude.

Table II-1 shows the flow capacities for some of the run conditions. The flow capacity of equal-diameter extraction-scrub and stripping columns is limited by the stripping column, in which the capacity is about 70% of the extraction-scrub column based on solvent flow that is common to both columns.

Efficiency data are shown in Table II-2. These indicate the best conditions to be 70 cpm with a limiting flow rate of 380 gal/(hr)(sq ft) based on the stripping column. Corresponding HETS* values would be 4.2 ft for uranium stripping, 2.1 ft for uranium extraction, and 4.1 ft for thorium scrubbing. Uranium-thorium separation factors were reported as being consistently greater than 10^4.

Further detail is presented on experimental conditions, column profile samples, and calculated incremental HETS and HTU† values.

(D. M. Paige)

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*HETS indicates height equivalent to a theoretical stage.

†HTU indicates height of transfer unit.

Section

III

Reactor Fuel Processing

Research and Development on Nonaqueous Processing

Volatility Processes

Volatility Processes for High-Enriched Fuels

The methods employed in the processing of reactor fuels containing highly enriched uranium differ from those used for low-enriched fuels in two major aspects: (1) Since the concentration of uranium in highly enriched fuel is low (< 20%), the initial step of the processing scheme involves separating the uranium from the fuel matrix and thereby freeing the uranium for subsequent recovery by volatility methods. This approach is not required in the case of low-enriched fuel. (2) Recovery of plutonium is not required for highly enriched fuels. Studies are currently being made on alloy fuels of zirconium-uranium and aluminum-uranium. Volatility processes are also being considered for stainless-steel cermet fuels containing enriched uranium dioxide.

URANIUM-ALLOY FUELS

A fluid-bed volatility process for the recovery of uranium from highly enriched uranium-alloy fuels is being developed at Argonne National Laboratory (ANL).[1,2] Current studies are being made with uranium-zirconium and uranium-aluminum alloys. The process employs three principal steps in which chemical separation of the fuel constituents is achieved by selective volatilization of chlorides and fluorides. In the first step, separation of the alloying and cladding material (aluminum or zirconium) from the uranium is achieved by reaction at approximately 350°C with hydrogen chloride gas while the fuel element is submerged in a fluidized bed of inert alumina particles. Separation of the alloying and cladding elements occurs by formation of volatile $ZrCl_4$ and $AlCl_3$. Uranium is converted to solid UCl_3 during the hydrochlorination step and, for the most part, remains associated with the fluid-bed material. However, a portion of the UCl_3 is entrained in the gas stream leaving the fluid-bed reactor, and therefore a packed-bed filter is employed in series with the fluid-bed reactor to ensure adequate retention of uranium within the system.

In the second step the UCl_3 in the fluid-bed reactor and packed-bed filter is converted to UF_4 by reaction with hydrogen fluoride gas. Recovery of uranium as UF_6 is achieved in the third step by the reaction between UF_4 and fluorine at 250 to 500°C.

Bench-Scale Studies

Initial work on the development of a fluid-bed fluoride-volatility process for enriched-alloy fuels was conducted in a 1½-in.-diameter fluid-bed reactor. These studies were concerned with defining the behavior of uranium in the system and with establishing conditions that would result in a minimal amount of unrecoverable uranium. The studies were directed mainly to (1) the determination of the behavior of uranium in its passage through the packed-bed filter during the hydrochlorination step and (2) the retention of uranium by the alumina beds after fluorination. A summary report has been issued describing the results of bench-scale investigations on the processing of zirconium-uranium-alloy fuel.[1] Most of these results have been previously reviewed in *Reactor Fuel Processing.*[3–6]

Demonstration tests in the bench-scale equipment[1] indicated that uranium losses by transport through the packed-bed filter during the hydrochlorination step can be consistently maintained at a value less than 0.2% by using a deep bed of −14 +20-mesh alumina particles

as the filter medium and by operating the filter at the lowest possible temperature (330°C for zirconium-alloy fuels and 200°C for aluminum-alloy fuels).

Uranium recoveries of greater than 99% of the uranium in the alloy charge were achieved[1] by conducting the fluorination as follows: carrying out the reaction for 0.5 hr at 250°C with an initial concentration of 5 to 10 vol.% fluorine in nitrogen, then raising the bed temperature to 500°C while gradually increasing the fluorine concentration, and fluorinating at 500°C with 90 vol.% fluorine for 2 hr to complete the reaction. A detailed analysis of the data from the bench-scale studies has indicated that the processing conditions which tend to increase the partial pressure of UF_6 in the gas stream during fluorination result in greater retention of uranium by the alumina bed. Conditions that appear to result in low uranium retention are: (1) operating at a low bed temperature during the initial fluorination period, (2) operating with low mass velocities in the gas stream during both the hydrochlorination and fluorination steps, and (3) operating the hydrochlorination step in such a manner as to produce a low reaction rate between uranium metal and HCl. The hydrochlorination conditions are significant in that they markedly affect the properties of the UCl_3 produced. Conducting the hydrochlorination reaction at high processing rates causes the UCl_3 product to appear as a fine particulate material that fluorinates rapidly, and thus a condition of high UF_6 partial pressure results.

Pilot-Plant Demonstration Tests

A pilot-plant facility has been constructed at ANL to demonstrate the processing of up to 20-kg charges of uranium-zirconium alloy and up to 14-kg charges of uranium-aluminum alloy.[2] A schematic diagram of the facility and a description of the process equipment were published in a previous issue of *Reactor Fuel Processing*.[4] In initial tests with uranium-containing fuel materials, it was shown that uranium recoveries of about 99% can be obtained using the processing conditions established in the bench-scale unit and that accurate uranium material balances can be achieved. A summary of operating conditions for the processing of both types of alloy fuels as established in recent runs[7] is shown in Table III-1.

A continuous hydrogen analyzer was employed in the off-gas system during the hydrochlorination reaction. This made it possible to monitor closely the progress of the reaction between the alloy and HCl and therefore to determine exactly when all the fuel material had reacted. From hydrogen-analysis data it was observed that the hydrochlorination reaction proceeds in two parts—a constant-rate period until approximately 70% of the alloy has reacted, followed by a period during which the rate continually decreases until all the alloy has reacted. During the constant-rate period, the HCl utilization is constant; during the falling-rate period the utilization efficiency decreases markedly. Therefore additional charges of alloy at the time when the reaction rate begins to diminish can produce a significant increase in the overall reaction rate and overall average utilization efficiency. This concept was evaluated in run 15, Table III-1. In this case three Zircaloy-uranium fuel subassemblies were successively charged to the fluid-bed reactor. The processing method involved charging the fuel subassemblies when about 60% of the previously charged material had reacted with HCl. By use of the successive-charging technique, a significant increase in HCl utilization efficiency and average reaction rate was observed, as compared with the values obtained in processing a single subassembly of Zircaloy-uranium alloy (run 13).

The following are several significant results from the pilot-plant runs:

1. During the hydrochlorination step processing rates near 3.0 kg/hr for both zirconium- and aluminum-alloy fuel assemblies were achieved. Cooling the reactor wall during the hydrochlorination step with an air-water mixture made it possible to maintain nearly isothermal conditions within the reactor even during periods of high reaction rates.

2. Making the depth of the packed-bed filter greater than 9 in. permitted the level of uranium particulate material passing through the packed-bed filter to be kept at less than 0.2% of the uranium in the charge.

3. The hydrochlorination reaction rate was virtually independent of temperature in the range studied during intervals in which HCl utilization was high; higher reaction rates with no concomitant decrease in HCl utilization efficiencies were observed at high fluidizing-gas velocities (~0.6 ft/sec) than were observed in

Table III-1 OPERATING CONDITIONS FOR FLUID-BED FLUORIDE-VOLATILITY PROCESSING OF UNIRRADIATED URANIUM-ZIRCALOY AND URANIUM-ALUMINUM FUEL SUBASSEMBLIES[7]

Inert-Bed Material
Reactor (6-in. Diameter): 40 kg Alcoa T61 Alumina (28 to 100 Mesh), 48-in. Static-Bed Height
Packed-Bed Filter (9-in. Diameter): 16 kg Alcoa T61 Alumina (14 to 48 Mesh), 11- to 12-in. Bed Height
Pyrohydrolyzer (6-in. Diameter): 10 kg of Final Bed from Previous Run with Similar Fuel, 20-in. Static-Bed Height

	Run 12	Run 16	Run 13	Run 15
Run charge				
Alloy type	Aluminum	Aluminum	Zircaloy	Zircaloy
Weight, kg	5.962	6.025	12.720 (9 plates)	20,380 (15 plates) 20,972 (16 plates) 15,038 (11 plates) 56,390
Uranium, g	280.5	273.6	117.0 ± 4	546.0 ± 10
Hydrochlorination data				
Reaction rate, kg/hr				
Average	0.92	0.87	1.39	2.06
Maximum	2.8	1.4	3.0	3.3
Reaction time, hr	6.5	6.9	9.2	27.4
Utilization efficiency, %				
Average	37.4	43.2	22.1	33.5
Maximum	65.0	67.0	53.0	59.0
Temperatures, °C				
Hydrochlorination step				
Reactor bed				
Average	360	364	360	372
Maximum	366	408	388	403
Element channel				
Average		380	370	377
Maximum		520	424	428
Reactor wall	350	351	347	355
Packed-bed filter	197	335	346	365
Pyrohydrolyzer bed	326	355	333	355
Hydrofluorination step (2 hr)				
Reactor bed	360	349	357	360
Filter bed	350	362	354	353
Fluorination step				
Reactor bed and packed-bed filter				
Reactor fluidized	250 to 500°C (7.5 hr)	250 to 500°C (2.8 hr)	250 to 500°C (6.2 hr)	250 to 500°C (2.4 hr)
Reactor static	500°C (2.0 hr)	500°C (3.0 hr)	500°C (2.1 hr)	500°C (2.1 hr)
Reactant concentrations, vol.%				
HCl in N_2	91	83.3	85	79
HF in N_2	21	20	35	17.5
F_2 in N_2				
Reactor fluidized	5	4.6	4.6	4.6
Reactor static	68	68	68	68
Gas velocity in fluid-bed reactor, ft/sec				
Hydrochlorination	0.39	0.40	0.44	0.42
Hydrofluorination	0.41	0.40	0.38	0.49
Fluorination				
Reactor fluidized	0.39	0.40	0.40	0.40
Reactor static	0.04	0.04	0.04	0.04

tests with gas velocities of 0.4 ft/sec; a satisfactory combination of high reaction rate and high HCl utilization was achieved by use of 80 vol.% HCl in N_2 as the feed gas to the reactor.

Studies with Irradiated Fuels

A bench-scale facility has been constructed at ANL for the study of the fluid-bed volatility process using highly irradiated alloy fuel materials of uranium-Zircaloy or uranium-aluminum.[8] The tests involving processing of irradiated fuel will define clearly the disposition of fission products and the total decontamination achieved in the process.

The facility shown in Fig. III-1 consists of a 1½-in.-diameter fluid-bed reactor and a packed-

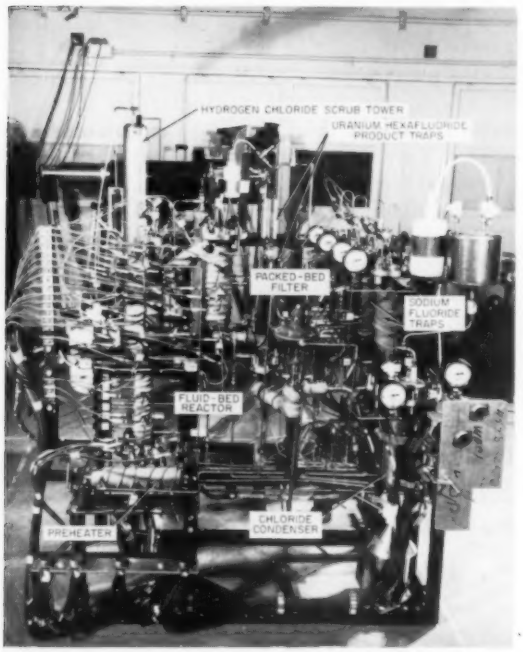

Fig. III-1 Fluid-bed volatility facility for studies with irradiated alloy fuels.[6]

bed filter with associated equipment for the containment of volatile chlorides and uranium hexafluoride produced in the process. Volatile zirconium tetrachloride or aluminum trichloride produced by reaction of the fuel alloy with hydrogen chloride is condensed to a solid chloride that is readily disposed by dissolution in dilute hydrochloric acid and subsequent solidification in cement. The uranium hexafluoride produced by reaction of uranium trichloride with fluorine is decontaminated by a sorption-desorption operation in a series of four sodium fluoride traps maintained at 400, 400, 100, and 20°C. The hexafluoride product is subsequently collected in a series of refrigerated traps. Disposal units for hydrogen chloride and fluorine gases are included in the facility. All liquid wastes generated in the process are solidified with portland cement before discharge from the hot cell. All equipment components have been designed for completely remote operation and maintenance.

Data on uranium decontamination and fission-product distribution have been obtained from two runs in which 269 g of long-cooled irradiated uranium–Zircaloy-2 alloy were processed in each run.[9] The alloy used in these runs contained 4.92 g of uranium and 3.28 g of fission products (40% burnup) and was cooled for five years. The original uranium enrichment was 93%.

Values of uranium recoveries and losses were compared with those obtained in runs with unirradiated alloy fuel. Apparently the behavior of uranium in both cases was essentially the same, and the presence of fission products had no marked effect on uranium recovery or loss.

Measurements of fission-product activity after the hydrochlorination step indicate that cesium, cerium, ruthenium, and strontium are nonvolatile during hydrochlorination. A small amount of these activities, however, is entrained and deposited along with $ZrCl_4$ in the condenser.

An examination of the fission-product distribution following the fluorination step shows that the bulk of the activities of cesium, cerium, ruthenium, and strontium remain in the reactor and packed-bed filter. Some entrainment of these materials had occurred since cesium and strontium were found in all the sodium fluoride traps. Antimony was found in the 400°C sodium fluoride traps in quantities too large to be accounted for by an entrainment mechanism. Of the total amount of antimony found, about half remained in the reactor and filter. The rest apparently volatilized and was sorbed by the first sodium fluoride trap. Molybdenum and technetium were nearly completely removed from the reactor and filter beds during the fluorination step. Both accompanied uranium and were collected with the uranium in the 100°C sodium fluoride trap.

The behavior of fission products in this process was as expected on the basis of previous work performed on a similar process, the molten-salt fluoride-volatility process, in which very high decontamination of uranium was demonstrated in a "hot" pilot plant.[9a] The current work on the fluid-bed process indicated that the same decontamination procedures are applicable for both processes. Thus the decontamination factor for uranium, from the principal fission-product activities, calculated from activities in the 100°C sodium fluoride trap, was about 1×10^4. Contamination of the product by gamma-active isotopes apparently was mainly due to entrainment. Preliminary data indicate that higher decontamination can be obtained by incorporating a step in which the UF_6

is desorbed from the sodium fluoride traps and passed through a sintered metal filter prior to collection in refrigerated condensers.

ENRICHED URANIUM DIOXIDE–STAINLESS-STEEL CERMET FUELS

A demonstration test has been made at ANL to explore the feasibility of recovering uranium from a UO_2–stainless-steel cermet fuel clad in stainless steel.[10] The processing scheme involved the chemical destruction of the stainless-steel cladding and matrix by reaction with HF-oxygen mixture at 550°C, followed by fluorination of the exposed UO_2 with fluorine at 250°C to 550°C. The test was carried out in a 1½-in.-diameter fluid-bed reactor with refractory alumina as the inert fluid-bed material. The fuel charge consisted of a four-plate miniature subassembly which was 0.7 in. by 0.5 in. by 8.37 in. long and which weighed 90 g. The fuel material was a cermet made of 18 wt.% UO_2–stainless steel (type 304).

Destructive oxidation of the stainless-steel cladding and matrix was carried out at 550°C for 4 hr with a reacting gas mixture of 40 vol.% HF–40 vol.% O_2–20 vol.% N_2. The subassembly was completely disintegrated at the end of the oxidation step. The bed was then reacted with fluorine for 11 hr using the following procedure: with the reactor bed fluidized at 250°C, the fluorine concentration is gradually increased from 2 to 90 vol.% in nitrogen over a 6-hr period, the temperature of the bed is raised from 250 to 550°C over a 3-hr period, and the reaction is completed by increasing the fluorine concentration to 95 vol.% and operating under static-bed conditions for 2 hr at 550°C.

High uranium recovery (> 99%) was indicated by the low quantity of uranium retained by the alumina at the end of the fluorination step. The residual uranium concentration in the alumina amounted to 0.005 wt.%, which corresponds to 0.2% of the uranium present in the charge.

Volatility Processes for Low-Enriched Fuels: Processing of UO_2 Fuels

A fluid-bed fluoride-volatility process is being developed at ANL[2] to recover uranium and plutonium from spent uranium oxide fuel. In this process uranium and plutonium oxides are fluorinated with fluorine to produce volatile uranium and plutonium hexafluorides that are subsequently decontaminated and separated from

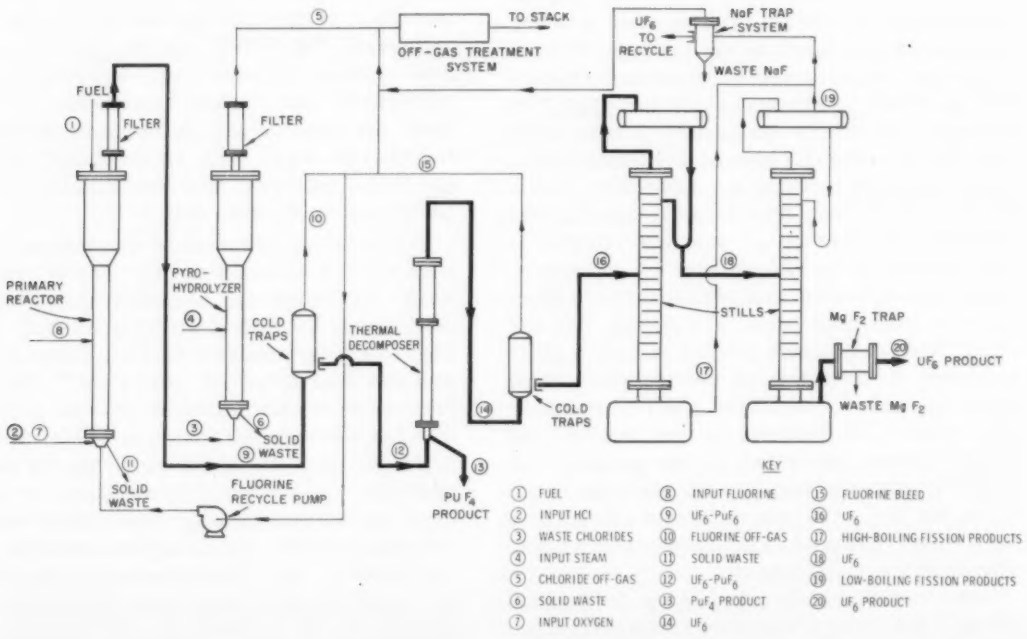

Fig. III-2 ANL fluid-bed fluoride-volatility process for UO_2-PuO_2 fuels.[11]

one another. Of major concern in the development of volatility processes is defining the behavior of plutonium during the separation steps and establishing methods for the recovery of plutonium.

FLUID-BED FLUORIDE-VOLATILITY PROCESS

A material flow sheet[11] describing the ANL fluid-bed fluoride-volatility process for the recovery of uranium and plutonium from spent oxide fuel is shown in Fig. III-2. In the process the Zircaloy-clad fuel (1) is introduced into the fluid-bed reactor and contacted with hydrogen chloride (2) gas. By reaction of the cladding with hydrogen chloride, the cladding is converted to volatile $ZrCl_4$. The $ZrCl_4$ is removed from the reactor to the pyrohydrolyzer wherein it is converted to a solid oxide (6) for disposal as a waste material. The oxide fuel, which remains unaffected by the decladding treatment, is contacted with oxygen (7) and fluorine (8) gas. The volatile fluorides (9), UF_6 and PuF_6, are condensed in a series of refrigerated condensers. The mixed hexafluorides are subsequently fed to a thermal decomposition reactor. Here the PuF_6 is decomposed and deposited as solid plutonium tetrafluoride (13), and the UF_6 passes through the unit to distillation columns for final decontamination (20). The progress of engineering-development work at ANL on this process has been reviewed in recent issues of *Reactor Fuel Processing*.[12,13]

RECOVERY OF PLUTONIUM FROM URANIUM DIOXIDE FUEL

In the fluid-bed fluoride-volatility process, declad fuel elements are reacted in a bed of alumina particles with oxygen and then with fluorine at about 500°C to convert the oxides to volatile UF_6 and PuF_6. Laboratory-scale investigations are being made at ANL[2] to define the conditions that result in a high degree of removal of UF_6 and PuF_6 from the fluidized alumina bed during fluorination of U_3O_8-PuO_2 mixtures. Mixtures of U_3O_8 and PuO_2 are being used in these studies to simulate the product that is formed by the oxidation of UO_2-PuO_2 fuel pellets. The U_3O_8-PuO_2 is mixed with alumina and conveyed to the reactor in the fluidizing gas stream and contacted with fluorine gas at a point just above that at which the powder enters the reactor. The fluorination reaction occurs as the streams mix.

A series of tests was performed (Ref. 2) to determine the feasibility of using one bed of alumina particles for the fluorination of several batches of feed material. Preliminary data indicate that, when recycle of the alumina bed material is incorporated, the overall plutonium recovery can be significantly increased as compared with the recovery obtained when single batches of feed are fluorinated and the bed material is then discarded. It was also observed in these tests that the plutonium retained on the alumina particles after fluorination was located exclusively on the surface of the particles.

ENGINEERING-SCALE FACILITY FOR UO_2-PuO_2 FUEL MATERIALS

An engineering-scale high-alpha facility is being constructed at ANL[2,14] to study steps in the processing of ceramic fuel materials by the fluoride-volatility process. The facility includes two alpha type boxes that were described in a previous issue of *Reactor Fuel Processing*.[15] The major process steps that will be studied in the facility include fluorination of the fuel, condensation of the hexafluoride products, separation of UF_6 from PuF_6 by thermal decomposition of PuF_6, conversion of mixed uranium and plutonium hexafluorides to oxides, and purification of UF_6 by distillation. All the plutonium-processing equipment is housed in the large alpha box, which is $17\frac{1}{2}$ ft high, $26\frac{1}{2}$ ft wide, and $3\frac{1}{2}$ ft deep. The smaller box, $10\frac{1}{2}$ by $12\frac{1}{4}$ by $3\frac{1}{2}$ ft, contains the process-gas metering manifolds and equipment for the scrubbing and filtration of the ventilation and process exhaust gases. A portion of the large glove box that contains equipment used for processing plutonium-containing material is shown[16] in Fig. III-3. All manual operations on processing equipment are carried out through glove ports.

The arrangement of the processing equipment in the large glove box is shown[14] in Fig. III-4. The equipment for demonstrating the distillation of UF_6 will also be installed in the large box. The fluorination system consists of a fluid-bed fluorinator with connected off-gas filters, a secondary off-gas filter, hexafluoride condensers, a pump for recirculating part or all the fluorine-containing process off-gas, a gas-analysis system, and chemical traps for removing fluorine and hexafluorides from the process exhaust gas. The fluorinator is constructed of welded Nickel 200. The fluidization section of the fluorinator consists of a 4-ft

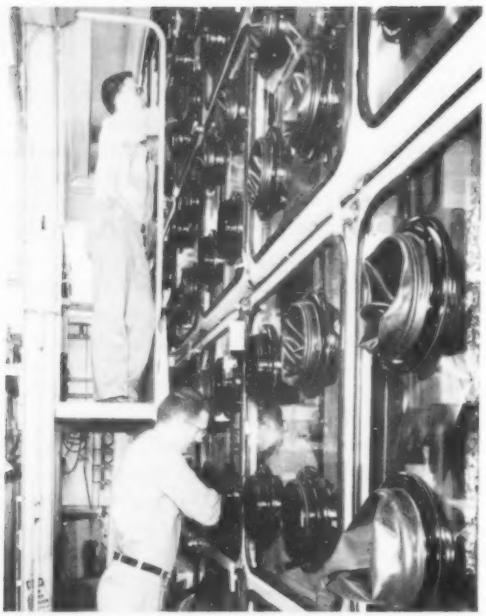

Fig. III-3 Large glove box of the ANL facility for engineering-scale studies of fluoride-volatility processing of plutonium-containing fuels.

section of 3-in. schedule-40 pipe. The disengaging section is in the form of an inverted, oblique, truncated cone, 20 in. long, with a top 14 in. in diameter.

The fluidized-bed converter reactor,[14] located in the box adjacent to the fluorinator, is to be used to study both the conversion of gaseous mixtures of UF_6 and PuF_6 to oxides and the separation of UF_6 from PuF_6 by selective thermal decomposition of PuF_6 to nonvolatile PuF_4. (A detailed description of the conversion of UF_6 to UO_2 in a similar fluid-bed reactor is presented in Sec. V of this issue of *Reactor Fuel Processing*.) The converter is fabricated of Inconel and consists of three sections connected by flanges: a conical bottom section, a 2-in.-diameter 24-in.-long fluid-bed section, and a 4-in.-diameter 24-in.-long cooling-filtering section.

The presence of volatile PuF_6 in the process has necessitated extra precautions in the design of the containment system. Complete details of the ventilation, scrubbing, and filtration facilities have been reported by Vogel, Carls, and Mecham.[14]

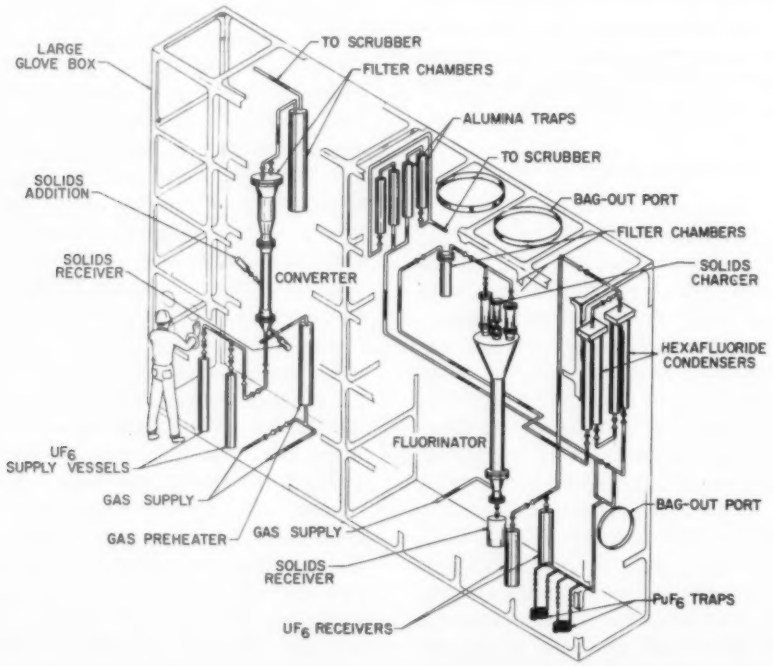

Fig. III-4 Overall view of process equipment in a large glove box.[14]

Preparation and Properties of Uranium Hexafluoride

The basis of all fluoride-volatility processes is the production of UF_6 by the reaction of a fluorinating agent with a uranium-containing material. Fundamental knowledge of the fluorination reaction is therefore of practical significance. In a study of the reactions of U_3O_8, UO_3, and UO_2 with fluorine gas, Iwasaki[17,18] observed that the reactions proceeded in two steps: (1) the conversion of the oxide to UO_2F_2 and (2) the conversion of UO_2F_2 to UF_6. In all cases the first-step reaction was found to be rapid in comparison with the second step. For the three oxides it was observed that the fluorination of the UO_2F_2 intermediate followed a linear rate law. Apparent activation energies of the second-step reactions for U_3O_8 and UO_3 were 21.3 and 22.0 kcal/mole, respectively.[17] The activation energy[18] of the second step for UO_2 was affected by the type of UO_2 powder and ranged from 33.1 to 29.4 kcal/mole.

Chlorine trifluoride has been used in several applications as a fluorinating agent for the production of UF_6 from uranium compounds. The reaction of ClF_3 with UO_2F_2 to produce UF_6 has been studied at the Paducah Gaseous Diffusion Plant.[19] Previous work, reported in *Reactor Fuel Processing*,[20,21] revealed that the reaction was first ordered with respect to UO_2F_2 in an excess of ClF_3 and that the reaction would proceed readily at 25°C and above. The experimentally derived[19] activation energy for the reaction was found to be 10.2 ± 0.5 kcal per mole of UO_2F_2. The combined effect of temperature and ClF_3 partial pressure on the specific reaction rate for UO_2F_2 with a surface area of 6 m^2/g can be described by the equation:

$$\log k = 6.5733 - 2.2321 \frac{100.0}{T} + 0.8261 \log P$$

where k is the specific reaction rate, $(1/\text{min}) \times 10^4$; T is the absolute temperature in degrees Kelvin; and P is the partial pressure of ClF_3 in millimeters of mercury.

The density of pure liquid UF_6 has been determined by Wertz and Hedge[22] over the temperature range 65 to 90°C. The density of UF_6 can be expressed as a function of temperature by the equation

$$\rho = 2.0843 - 0.0031t + 0.3710\,(230.2 - t)^{0.3045}$$

where ρ is the density of UF_6 in grams per cubic centimeter and t is the temperature in degrees centigrade. It was observed that the densities of uranium hexafluoride of various isotopic compositions, measured relative to the density of natural uranium hexafluoride, vary directly as the molecular weight.

Decontamination of UF_6 produced by fluoride-volatility techniques can be accomplished by an absorption-desorption cycle in a bed of NaF pellets. The results of a study of the kinetics of the reaction between UF_6 and NaF have been reported recently by Peka.[23] The parameters affecting the rate of sorption and the total capacity of NaF pellets when used for UF_6 collection have been studied by workers at Oak Ridge National Laboratory (ORNL) to provide design information for sorption beds.[24] The experimental program evaluated the effects of pellet specific surface area, pellet void fraction, and temperature on UF_6 sorption behavior. The data showed that the effective capacity of the pellets for UF_6 decreases with increasing temperature (from 0.8 g of UF_6 per gram of NaF at 30°C to 0.35 g of UF_6 per gram of NaF at 150°C for pellets having a specific surface area of 1.0 m^2/g). The effective capacity decreases markedly with increasing specific surface area (from 1.05 g of UF_6 per gram of NaF at 100°C for a specific surface of 0.7 m^2/g to 0.25 g of UF_6 per gram of NaF at 100°C for a specific surface of 1.15 m^2/g). Capacity of the pellets was observed to decrease sharply as the void fraction decreased; high absorption capacity (1.3 to 1.6 g of UF_6 per gram of NaF) was observed in the temperature range 30 to 220°C using pellets with a void fraction of 0.50, whereas negligible sorption was observed (0.1 to 0.2 g of UF_6 per gram of NaF) over the same temperature range with pellets having a void fraction of 0.35. (J. Barghusen)

Corrosion in the ORNL Molten-Salt Fluoride-Volatility-Process Pilot Plant

A summary of data on corrosion of the hydrofluorinator and fluorinator of the ORNL volatility pilot plant has been published.[25] In these process runs the hydrofluorinator is used for the dissolution of zirconium-uranium-alloy fuel in a $NaF-LiF-ZrF_4$ molten-salt mixture at 500 to 650°C by sparging with hydrogen fluoride gas. The molten salt containing dissolved uranium (as UF_4) is transferred to the fluo-

rinator vessel where the salt is sparged with fluorine gas at 500°C. In the fluorination the uranium (UF_6) is separated as the volatile hexafluoride from the salt that retains the bulk of the fission products as nonvolatile waste. In the present study the corrosion results were reported for 40 processing runs with both irradiated and nonirradiated zirconium and Zircaloy-2-clad fuel elements.

The hydrofluorinator was made of INOR-8 (71 wt.% nickel, 16 wt.% molybdenum, 7 wt.% chromium, 5 wt.% iron), and the fluorinator was made of low-carbon nickel (Nickel 201). Wall-thickness measurements were made primarily by ultrasonic measuring devices. Pitting, cracking, and intergranular corrosion were studied visually with telescopes and mirrors, by radiography, by wax impressions, and by removal and examination of specimens taken from the equipment walls. Corrosion data from specimen rods, including those from other alloys that have potential as construction material for reaction vessels, were obtained.

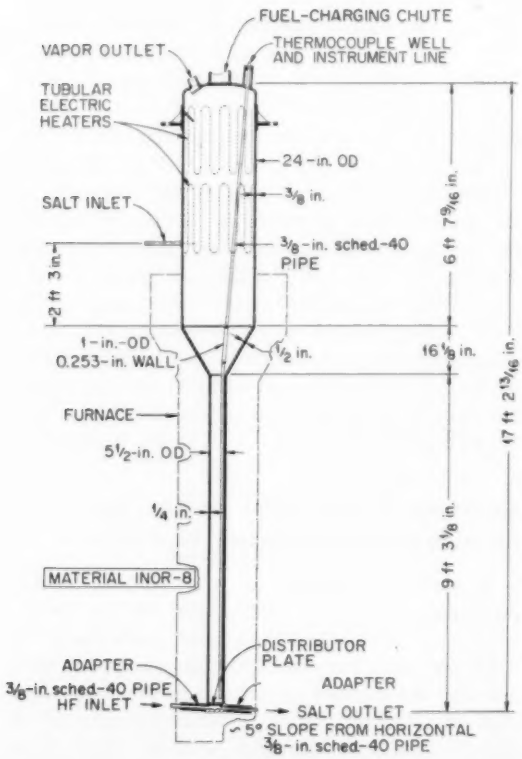

Fig. III-5 Volatility-pilot-plant hydrofluorinator.[25]

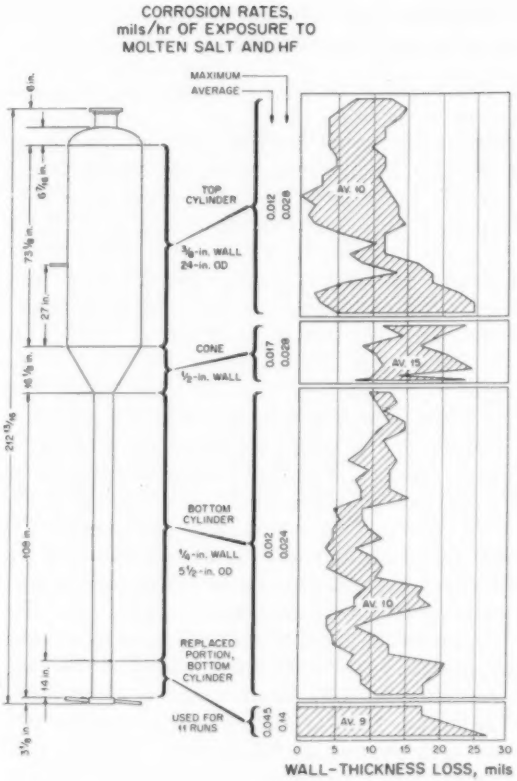

Fig. III-6 Hydrofluorinator wall-thickness loss during 40 zirconium processing runs.[25]

Typical run time in the hydrofluorinator was 69 hr; of this time the alloys were exposed to molten salt for 28 hr and to molten salt and hydrogen fluoride for 24 hr. Maximum bulk-metal losses in the hydrofluorinator ranged from 0.028 to 0.14 mil per hour of exposure to hydrogen fluoride. For maximum pitting attack a value of 0.5 mil/run was estimated from the data. The total attack was estimated as 3.6 mils/run, based on the maximum corrosion rates. The hydrofluorinator vessel was constructed with 125-mil corrosion allowance, and its estimated minimum lifetime is 35 runs, based on the above figures for maximum corrosion. However, if the present state of the vessel is considered, a more favorable lifetime could be estimated, namely, in the range of 68 to 125 runs. A diagram of the hydrofluorinator is shown in Fig. III-5, and measured corrosion losses for various portions of the vessel are shown in Fig. III-6.

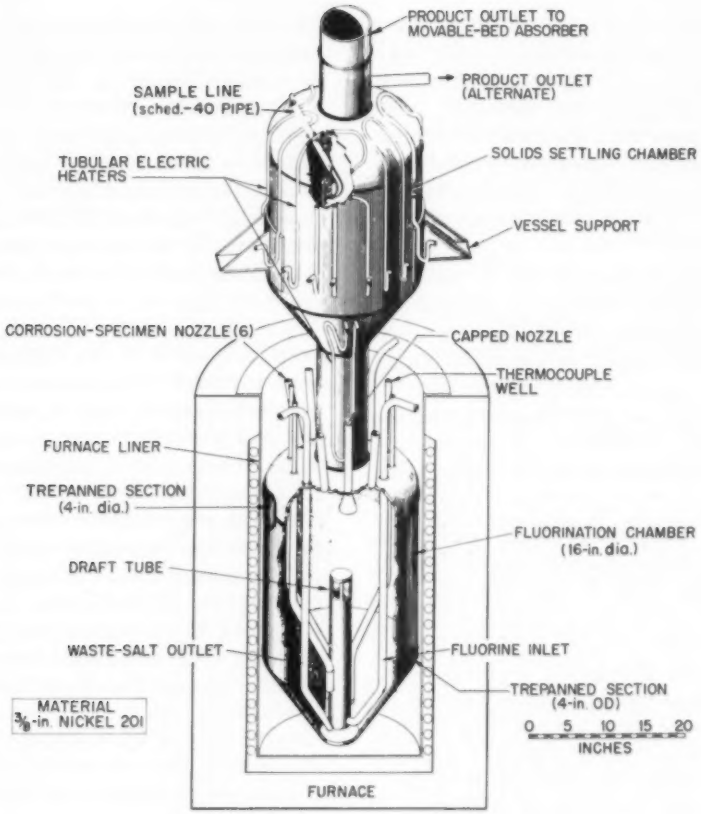

Fig. III-7 Volatility-pilot-plant fluorinator, Mark III.[25]

As indicated in Fig. III-6, a bottom portion of the hydrofluorinator was replaced during the series of runs. Cracks had developed in this portion of the vessel after 29 runs. Because the vessel had been fabricated by welding together a number of sections, most of which did not develop cracks, the failure of the bottom portion was attributed to a substandard alloy.

Typical run time for the fluorinator was 96 hr, of which 58 hr involved exposure to molten salt and 2 hr involved fluorine sparging. The maximum corrosion rate observed for the Nickel 201 of the present fluorinator was 0.9 mil per hour of fluorine exposure. This maximum rate was found in the vapor region and was determined from wall-thickness measurements made after the first 14 runs. Pits of up to 10 mils (total) were also observed for the same period. No metallurgical examination (required to measure intergranular attack) was made for the vapor portion of the fluorinator; however, specimens removed from the lower portion (which had been exposed to molten salt) showed a maximum attack of 0.56 mil per hour of fluorine exposure, including intergranular attack on both internal and external surfaces of the vessel. An overall corrosion rate of 1.2 mils per hour of fluorine exposure was estimated as a basis of predicting vessel lifetime. For the 175-mil corrosion allowance of the vessel, the estimated lifetime was 73 runs. A diagram of the fluorinator is shown in Fig. III-7.

Further analysis of corrosion is to be made from results obtained at ORNL and Battelle Memorial Institute. (W. J. Mecham)

Compact Pyrochemical Processes

Compact pyrochemical processes are nonaqueous processes for the recovery and

purification of partially burned reactor fuels. Hitherto these processes have been called "pyrometallurgical processes." The processes have been renamed "compact pyrochemical processes" to emphasize their utility for recovery of ceramic fuels (for example, oxides and carbides), as well as metallic fuels, and their suitability for use in small plants serving a few or even one reactor.

In the processes extensive use is made of molten-metal and -salt systems as processing media. The metal solvent systems consist principally of various alloys* of zinc, cadmium, magnesium, and copper. The salt systems are halide salts of alkali and alkaline-earth metals. Metallic fuels are sometimes processed directly, i.e., without dissolution in any solvent media.

The desirable features of these processes include (1) their ability to accommodate short-cooled high-burnup fuels of both ceramic and metallic types with consequent reduction in fuel inventory, (2) small process volumes which make them suitable for use in a small plant, (3) decrease in criticality problems because of the absence of aqueous solutions, and (4) the direct production of concentrated fission-product wastes. These features should be economically beneficial, particularly in fast reactor fuel cycles.

EBR-II Fuel Cycle Facility and Operations

The Experimental Breeder Reactor No. 2 (EBR-II) complex of ANL at the National Reactor Testing Station, Idaho, represents the first practical demonstration in the U. S. nuclear power program of the integrated operation of a nuclear power reactor and a nuclear fuel processing and refabrication plant (Fuel Cycle Facility) located adjacent to it. In this operation the partially spent fuel elements from the EBR-II reactor are processed, fortified with ^{235}U, refabricated by remote means in the Fuel Cycle Facility, and then returned to the EBR-II reactor to close the fuel cycle. This facility will provide the cost information necessary to permit economic evaluation of the closed cycle and of the new methods of processing and refabricating reactor fuels.

*Usually binary alloys.

A high-temperature process known as melt refining,† which was developed at ANL, is being successfully used in the Fuel Cycle Facility for the remote recovery and purification of discharged irradiated fuel materials from the EBR-II reactor. Purified ingots of uranium fuel material resulting from the melt-refining step have been refabricated into individual fuel elements ready for incorporation into a finished fuel subassembly for use in the EBR-II reactor.[26]

The first batch of partially spent EBR-II reactor fuels was successfully processed by melt refining[27] in September 1964. The reactor was subsequently shut down because of mechanical difficulties. Consequently the next batch of fuel was not discharged for processing until February 1965. At that time 10 kg of fuel (147 fuel pins) with an average burnup of 0.15 at.% was processed by melt refining with a resulting ingot yield[28] of 94.4%. The third melt-refining run of irradiated fuel was made in March 1965. The charge consisted of 8.4 kg of partially spent fuel (135 fuel pins) plus uranium-bearing radioactive scrap from the previous two melt-refining runs to make 11.6 kg. As before, the operation proceeded smoothly, giving a product ingot with a yield[30] of 94.5%.

Additional experience in fuel refabrication is being gained by reclaiming unirradiated fuel elements from the disassembly of special assemblies prepared for dry and wet critical and related operations. A total of 2417 fuel pins have now been canned, bonded with sodium, and inspected, i.e., placed inside stainless-steel cans with sodium, welded tight, and tested for leaks. The total number of acceptable elements obtained was 2233. The principal cause for rejection was an indication of the presence of bubbles or voids in the sodium bond between the fuel pin and can. Other causes included damaged tips, sodium levels not as specified, leaks in welds or jackets, inadequate data, and damages occurring in testing and assembly.[31]

†In melt refining the fuel material is melted at about 1400°C in a zirconia crucible where certain fission-product elements are removed by volatilization and certain others are removed by selective oxidation reactions with the crucible material.[29] These oxides are retained in a residue (or skull) that remains in the crucible when the purified metal is poured. The residue contains between 5 and 10% of the total fuel charge and so must be separately processed for recovery and purification of the contained uranium.

In-cell lighting of the EBR-II Air Cell and Argon Cell is provided by ninety-six 1000-watt mercury-vapor lamps.[32] This lighting has proved to be very satisfactory. In the 30 months that they have been in use, no lamp has burned out. Most of the lamps have given about 17,000 hr of service. In the Argon Cell, which has 72 lamps, the illumination along the center line of the cell working area has decreased from an initial value of 180 ft-candles in August 1962 to a value currently estimated to be about one-half the initial value. (In February 1963 this illumination value was 125 ft-candles.) Since the present level of illumination makes certain operations difficult, and also as insurance against lamp burnout, preparations are being made to replace lamps.[33]

Since the most recent entry by personnel into the Argon Cell, approximately one year of highly satisfactory operation in the inert atmosphere has been experienced. At differential pressures of 2 to 3 in. H_2O below atmospheric, inleakage of air has typically been held to 0.2 to 0.3 cu ft/hr, and the purity of the atmosphere has been maintained in the range of 30 to 60 ppm oxygen, 25 to 50 ppm water vapor, and about 5% nitrogen. Typical consumption of argon gas, including that required for purging of transfer locks, has been about 3500 cu ft/week.[28]

In connection with installation of future processes in the Fuel Cycle Facility, a need exists for structural metals that will withstand limited exposures at 900°C to the argon–5% nitrogen atmosphere of the Argon Cell. Eight metals (Inconel 600, Inconel 800, Hastelloy C, Hastelloy X, type 304 stainless steel, type 316 stainless steel, tungsten, and molybdenum–30% tungsten alloy) have been evaluated by exposure at 900°C to argon–5% nitrogen for 1000 hr. The two Inconel alloys and the two Hastelloy alloys were somewhat embrittled; thus the useful lifetime of these alloys was possibly limited in the Argon Cell atmosphere. The usefulness of tungsten, molybdenum–30% tungsten, type 304 stainless steel, and type 316 stainless steel was not impaired by the 1000-hr exposure.[31]

EBR-II Skull-Reclamation Process

One of the auxiliary processes used in the EBR-II fuel cycle is the skull-reclamation process for reclaiming uranium from melt-refining residues. In the skull-reclamation process, the uranium product is recovered and purified by selective oxidations and reductions and associated transfers between zinc-magnesium solvent and a halide-salt flux, followed by fractional crystallization of the uranium from the solvent metals, and final recovery of the product uranium as a metal by evaporation of the solvent metals.[29] The skull-reclamation process is in the final stages of engineering development. When its development has been completed, the skull-reclamation-process equipment will be installed in the EBR-II Fuel Cycle Facility.

Engineering-Scale Development

The engineering development of the skull-reclamation process has been done on a 1.5-kg uranium-charge basis in a nitrogen-atmosphere glove box in the Chemical Engineering Division of ANL.[34] Special attention has been given to achieving adequate uranium recovery in this process. A uranium recovery of about 95% will suffice because only a small sidestream of fuel (5 to 10% of the total) is processed through the skull-reclamation process.[29,35] In some of the earlier runs, there was excessive entrainment in the phase transfer that followed precipitation of uranium-zinc intermetallic precipitate. In one case as much as 18% of the uranium charged[35] was transferred in the waste supernatant-metal solution. To overcome this, measures have been taken to produce a well-settled precipitate bed. The major operating change allows longer settling of the precipitate prior to transfer of the supernatant metallic solution. This has reduced uranium entrainment[28,30] to 1 to 2%.

While the operating variables for the skull-reclamation process are being optimized, the fabrication of a full-scale skull-oxide-reclamation furnace (Fig. III-8) has been completed. The furnace will be resistance heated and will accommodate a 14-in.-ID pressed-and-sintered tungsten crucible (Fig. III-9). Preliminary heat tests of this furnace and the testing of auxiliary equipment components, such as a stirrer and transfer line (both fabricated of molybdenum–30 wt.% tungsten), have been completed satisfactorily.[31,33]

Rotating Step

The final operation in the skull-reclamation process is the retorting step, in which the

Fig. III-8 Full-scale skull-oxide-reclamation furnace.[34]

uranium-metal product is separated from the residual solvent metals by vaporization of the solvent metals.[29] In this step the magnesium-zinc is distilled at 800 to 900°C, after which the residual uranium is removed from the crucible for refabrication. In a previous flow sheet uranium consolidation was to be accomplished by melting the uranium at about 1200°C in a beryllia crucible. Beryllia crucibles have desirable characteristics for use in this step of the skull-reclamation process[35] since they do not react significantly with the solvent metals magnesium or zinc, or with molten uranium, which is the product of the retorting operation. In work to date, beryllia has not been wetted by uranium, which indicates that the product might be removed from the crucible as a solid ingot. However, fabricators have been unable, as yet, to produce a structurally sound plant-size crucible.[35] Therefore the possibility of using a tungsten crucible in the retorting step is being investigated.

The proposed use of tungsten crucibles is based on the fact that, although the residual uranium sticks to the surface of the crucible, operation at the maximum retorting temperature of 900°C results in little or no attack on tungsten crucibles.[34,36] Therefore, if a method can be found for removing the uranium from the crucible surface after vaporization of the zinc and magnesium without exceeding 900°C, the use of a tungsten crucible for retorting would be practical. One possible means of accomplishing this is by converting the uranium to the hydride, followed by dehydriding. It is also possible that hydrided-uranium product, rather than uranium metal, can be the final product of skull processing and would be suitable for return to the melt-refining step.[34]

Two retorting runs, carried out in a tungsten crucible in a modified melt-refining furnace, were made to prepare hydrided-uranium product for testing its use as recycle material to the melt-refining operation. Although the re-

Fig. III-9 Pressed-and-sintered tungsten crucible, 16 in. in outside diameter by 24½ in. tall, for skull-reclamation process. (Courtesy of D. Grosvenor, Chemical Engineering Division, Argonne National Laboratory.)

torting operation itself requires further development work, the hydriding operation went very well and yielded a product that was readily poured from the tungsten crucible. After this material was mixed with unirradiated depleted uranium – 5 wt.% fissium and a small amount of sodium, the hydrided material was decomposed, and the entire charge was melt refined with a poured yield[31] of 93.0%. These results indicate that in routine plant operations, there should be no problem in mixing hydrided material with spent fuel pins and then melt-refining the mixture.

A plant-size retorting apparatus has also been completed.[31] In this equipment, charges of zinc-magnesium (no uranium) were distilled from a graphite crucible at reduced pressure and at a temperature of about 750°C. The metal distillation rate was close to the design figure of 100 g/min with a 30-kg charge.[30]

Crucible Development for Skull-Reclamation Process

Two tungsten crucibles are presently being employed in the EBR-II skull-reclamation process.[30] One crucible, of relatively large size (15 in. in inside diameter by 30 in. high), is used for the bulk of the process steps, i.e., those steps between the oxidation of melt-refining crucible skulls (to obtain a free-flowing powder) and the retorting of the uranium-magnesium-zinc solution to recover uranium-metal product; the other crucible, of smaller size (7½ in. in inside diameter by 17 in. high), is used for the retorting step (see the preceding subsection). The tungsten crucibles used to date have been made by pressing and sintering and have given good performance. However, because the method of fabrication results in crucibles with thick walls, the crucibles are heavy and unwieldy. Alternative methods of fabrication, which might overcome the disadvantages of pressed-and-sintered tungsten crucibles, are therefore being examined.[30]

A promising alternative technique is the fabrication of a freestanding tungsten crucible by plasma-spraying tungsten on a removable mandrel, followed by sintering the crucible at a high temperature for densification. Such a crucible would have properties similar to the pressed-and-sintered crucible now in use. It would not be limited in size, but would have a thinner, more uniform wall and would probably cost less. A small freestanding plasma-sprayed crucible (4 in. in outside diameter by 6 in. high by 3/16 in. in wall thickness) successfully contained a zinc-magnesium mixture and EBR-II halide-process salts at 800°C for periods up to 4½ hr with no evidence of leakage.[30]

The investigation of two other alternative crucible-fabrication methods has recently been completed. These are (1) plasma-spraying a tungsten coating on the inside of a silicon carbide substrate* and (2) welding. The first method results in a porous crucible since silicon carbide will not withstand the temperature (1350°C) required to close the tungsten pores by sintering.[30] Welding, by present techniques, is also unsatisfactory[35] because of the difficulty in obtaining complete penetration and because the resulting grain growth and accompanying embrittlement suffered by the tungsten materially weaken the crucible at the weld.

Processes for Advanced Reactor Fuels

Compact pyrochemical processes are under development at ANL for processing fast breeder reactor fuels of the ceramic (e.g., oxide and carbide) or metallic types.[30] These processes involve the separation of uranium and plutonium from fission products by two major operations: (1) selective oxidation of uranium and plutonium (and the more easily oxidized fission products) to chlorides and their transfer to a molten-halide-salt phase, leaving in the metal phase the relatively noble fission products such as ruthenium, molybdenum, palladium, and technetium, and (2) selective reduction of uranium and plutonium to the metals and their transfer from the salt phase to a solvent-metal phase, leaving in the salt phase the highly reactive fission products (rare earths and alkaline earths). Uranium and plutonium metals are recovered from the product solution by vaporizing the solvent metals. The uranium and plutonium may then be converted to the desired type of fuel by conventional procedures.[30] Solvent metals currently under investigation include cadmium to which small amounts of magnesium are added[30] and a copper-base alloy containing various amounts of magnesium.[31]

*The number of possible substrate materials is limited since the thermal-expansion coefficients of tungsten and the substrate must match to ensure good adherence of the tungsten to the substrate.

Cadmium-Base Solvent

The flow sheet for the purification process[34] that utilizes a cadmium-base solvent is given in Fig. III-10. In this process cadmium chloride is employed as the oxidizing agent; magnesium, sodium, and potassium in a cadmium-magnesium alloy are employed as the reducing agents. The composition of the molten-salt phase is 30 mole % NaCl, 20 mole % KCl, and 50 mole % $MgCl_2$. In the step in which uranium and plutonium are to be selectively oxidized to the chlorides, it was found that the molten chloride can be maintained at the desired composition and that it can accommodate UCl_3 concentrations up to 30 to 35 mole % at the proposed operating temperature of 600°C. Subsequently, the uranium can be reduced by sodium-potassium-magnesium (in liquid cadmium) in the proper proportion to regenerate the 30 mole % NaCl–20 mole % KCl–50 mole % $MgCl_2$ salt. The reaction proceeds smoothly, and reduction of UCl_3 is essentially complete.[30]

The cadmium in the noble-metal waste solution can then be vaporized and collected for recycle; the salt solution containing the rare-earth fission products can be purified by extracting the fission products into an aluminum-magnesium alloy, which is then discarded as a waste. This consolidates the fission products into a small volume of metal for storage.[30] The cadmium chloride oxidizing agent can be regenerated from recycled cadmium solvent by chlorination at 500°C in the presence of the molten salt. This procedure[30] has yielded $CdCl_2$ concentrations in the salt of up to 60 mole %.

For the proposed waste-concentration step, distribution coefficients (concentration in salt/concentration in metal) and solubilities[31] have been determined for representative rare earths between 30 mole % NaCl–20 mole % KCl–50 mole % $MgCl_2$ and aluminum-magnesium alloys at nominal magnesium concentrations of 13, 20, and 30 wt.% and at temperatures of 500 to 900°C. Solubilities and distribution coefficients for aluminum–20 wt.% magnesium at selected temperatures are as follows:

Element	Solubility, wt.%		Distribution coefficient	
	500°C	600°C	550°C	600°C
Yttrium	0.91	3.45	2.42×10^{-3}	4.39×10^{-3}
Cerium	2.24	3.27	4.12×10^{-4}	7.08×10^{-4}
Praseodymium	2.53	3.91		4.4×10^{-4}

Aluminum pickup by a NaCl-KCl-$MgCl_2$ salt during a distribution experiment with aluminum-

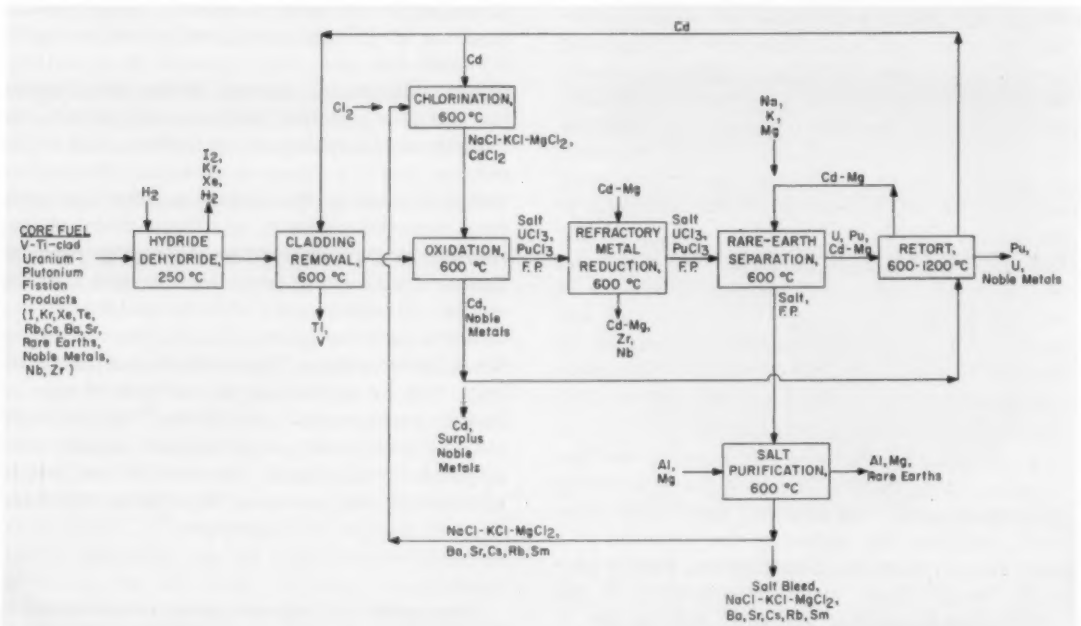

Fig. III-10 Flow sheet for cadmium-base solvent process.[34]

magnesium was sufficiently small (0.0015 to 0.005 wt.%) so that negligible aluminum contamination would result if this salt were recycled to process uranium and plutonium. These data indicate that aluminum-magnesium alloy should be a very satisfactory medium for the reduction and consolidation of rare-earth fission products.[31]

An engineering-development program for this process is also under way at ANL. This program is presently concentrated on studies of mass-transfer rates between liquid-metal and liquid-salt phases at high temperatures. The objectives are to demonstrate the feasibility of continuous metal-salt extractions, to determine optimum operating conditions, and to obtain a clearer understanding of the extractive process.[28]

Experimentally the rate of uranium transfer from a liquid cadmium–3.5 wt.% magnesium alloy into 20 mole % KCl–30 mole % NaCl–50 mole % $MgCl_2$ salt at 550 to 600°C was determined when the metal was passed through the static salt in packed columns. The overall mass-transfer coefficient, based on the salt phase, indicates a height for one theoretical stage of 2 to 5 ft for a typical packed extraction column in which plutonium* would be separated from the rare earths. Stage heights in the above range would be satisfactory.[28]

Studies of a mixer-settler extraction process have also begun. In experiments made to determine the mixing time and degree of agitation required for the extraction of cerium (a representative rare earth) from a cadmium–11 wt.% zinc–5 wt.% magnesium–3 wt.% cerium alloy into the $MgCl_2$–30 mole % NaCl–20 mole % KCl salt at 600°C, it was found that complete transfer of cerium from the metal phase to the salt phase could be attained by a few minutes of moderate to vigorous agitation.[30]

Work is also being carried out on the selection of materials for the cadmium solvent process. Various stainless steels and refractory compounds are being examined as container materials. Specifically, the corrosion resistance of type 405 stainless steel to the system having a metal phase of 81.4 wt.% cadmium–10.9 wt.% zinc–5.4 wt.% magnesium–2.3 wt.% uranium and a salt phase of 50 mole % $MgCl_2$–30 mole % NaCl–20 mole % KCl has been investigated. When the salt was thoroughly dried by pretreatment with a magnesium-cadmium solution, the depth of corrosion after exposing the type 405 stainless-steel test coupons in four positions (in the metal phase, at the metal-salt interface, in the salt phase, and in the vapor phase) for 225 hr at 650°C was below the limit of detection, i.e., less than 0.5 mil. Although the exposure time was short, type 405 stainless steel has excellent promise of being a satisfactory container material.[33]

*It is assumed that uranium and plutonium have the same mass-transfer coefficients.

Copper-Base-Alloy Solvent

The copper-magnesium–30 mole % NaCl–20 mole % KCl–50 mole % $MgCl_2$ system is of particular interest because, unlike other systems studied to date, it offers the possibility of uranium-plutonium separations by liquid-liquid extraction.[31] This system also offers the possibility of separating uranium-plutonium from fission products. Determinations of the codistribution behavior of uranium, plutonium, and praseodymium between copper-magnesium alloys and the salt system have been made at 500 to 800°C. It was found that praseodymium distributes strongly to the salt phase at low magnesium concentrations and that plutonium and uranium favor the metal phase, the uranium more strongly than the plutonium. With 20 wt.% magnesium in the metal phase, the separation factors (ratios of distribution coefficients) are as follows at 800°C:

	Separation factor
Uranium-praseodymium	5600
Uranium-plutonium	33
Plutonium-praseodymium	170

These data suggest that an adequate separation of rare-earth fission products from uranium and plutonium is possible by a single-stage extraction.[31]

Other Pyrochemical Purification Processes

A fused-salt–liquid-metal method for decontaminating a magnesium–40% thorium alloy containing yttrium, alkali, alkaline-earth, and lanthanide fission-product elements by selective oxidation-reduction reactions has been developed by Klepfer of Iowa State University.[37] In this scheme a KCl–44.5% LiCl eutectic salt

containing $MgCl_2$ is used to selectively oxidize those elements whose free energies of formation are greater than that of magnesium chloride. Yttrium and the lanthanide elements are effectively reduced from the salt in concentrated form by a zinc-magnesium scrub alloy. The optimum reducing power of the scrub alloy has been observed to be from 6 to 8% magnesium in zinc.

Simultaneous contact of the three phases was made in a single-stage batch extractor. At 600°C the transport of yttrium, cerium, neodymium, and samarium from the magnesium–40% thorium alloy through the salt phase to the supernatant zinc-magnesium scrub alloy was observed. Decontamination of the magnesium-thorium alloy to less than 20 ppm for each solute was attained in less than 10 hr. Thorium loss was very small.

Both the oxidation and reduction reaction equilibria are more favorable at low temperatures. The optimum magnesium chloride concentration in the salt depends on the impurity composition of the magnesium-thorium, relative phase weights, allowable thorium loss, and overall extraction time. It is estimated that from 10 to 25% $MgCl_2$ will permit practical process design.

Teitel and Layne[38] describe a method for purifying uranium metal without taking up the uranium into the purifying agent. In this method the uranium is intimately contacted with at least an equal weight of a molten magnesium-copper alloy for at least 1 hr. The alloy consists of at least 30 wt.% magnesium, 20 wt.% copper, and not more than 10 wt.% of other metals.

The work previously reported by Hanson[39] of Atomics International on the separation of thorium from thorium-magnesium alloys by the use of liquid lithium at 500 to 600°C has been successfully extended to thorium-zinc and uranium-zinc systems.[40]

Preparation of Metals by Reduction of Their Compounds

Curtis of Hanford has reported previously[41] on the successful demonstration of continuous electrowinning of plutonium metal from molten plutonium trichloride. He now reports[42] that continuous runs greater than 10 hr in length have been made in equipment with a favorable nuclear geometry (i.e., equipment that provides positive controls to avoid criticality). Currently the process produces 50 g of plutonium per hour, with a cathode-current efficiency of 60%. The process operates at 800°C and is contained in a 2-in.-diameter cylindrical ceramic-oxide cell. The best material tested for this cell is a slip-cast magnesia–10% titania body. This process is described in detail in Sec. V of this issue.

Miscellaneous

Jansen of Hanford presented a study[43] on the economic effects of varying the fission-product decontamination in a plutonium reactor at steady state. For a model close-coupled recycle system, he determined the effect of nonremoval of each fission-product nuclide during intercycle processing as a function of decontamination factor (DF). Estimates of the value of the neutrons lost to removable poisons indicate that DF's of 3 and 10 for all fission products in the model recycle system result in a loss of neutrons valued at $8 and $2, respectively, per kilogram of fuel per fuel cycle. Comparison of these losses with processing costs projected for plutonium-recycle reactors shows that from an economic standpoint a DF of 3 is probably low, whereas a DF of 10 is more attractive and may be satisfactory.

A study of plutonium-magnesium diffusion was presented by Craeynest and Calais.[44] Another fundamental study, of less pertinence as regards current processes, but possibly of interest in advanced processes, is the work of Delimarsky and Roms[45] on the solubility of bismuth in fused bismuth chloride.

A compilation of the existing theory of three continuous zone-refining systems: the zone-void system, the zone-transport system, and the molten-transport system, has been presented by Kennedy and Parke.[46] (L. Burris, Jr.)

Other Nonaqueous Processes

Compact, high-temperature processes are being developed for the recovery of fissile and fertile material from irradiated oxide and carbide fuels. Gases and molten salts are generally used as reagents and reaction media for high-temperature chemical conversions used in processes of this type. Since these materials

are not subject to significant radiation damage, such processes are particularly suited to closed-cycle low-decontamination processing of short-cooled high-burnup fuels.

Oxide-Fuel Processing

Development studies on the salt-cycle process for mixed uranium dioxide–plutonium dioxide fuels are continuing at the Pacific Northwest Laboratory (formerly Hanford).[47] In this process a mixture of powdered U_3O_8, PuO_2, and fission-product oxides is dissolved in molten chloride salt, and separation of uranium, plutonium, and fission products is achieved by electrolytic and chemical precipitation methods. In the separation of uranium from plutonium by selective electrodeposition of the dioxides, pyrolytic graphite was found to be greatly superior to AUG mold graphite as an anode material.

Work is continuing[47] on the preparation of uranium dioxide containing 2 wt.% plutonium dioxide for recycle to the Plutonium Recycle Test Reactor. About 12 lb of specification-grade mixed oxide has been prepared by electrodeposition from a lithium chloride–potassium chloride salt solution at 500°C. During the electrodeposition the salt was sparged with a 50% oxygen–50% chlorine mixture. Earlier scouting studies had shown no separate plutonium dioxide phase in electrodeposited mixed oxides containing 1.2 and 7 wt.% plutonium dioxide.

A patent[48] has been issued for a process developed at Hanford in which pure plutonium dioxide is recovered from a molten lithium chloride–potassium chloride (or sodium chloride) solution of uranium, plutonium, and rare earths. The plutonium dioxide is selectively precipitated by sparging the salt solution with chlorine while introducing oxygen or stannic oxide. Development work on this procedure was summarized previously.[49–52]

General progress on the salt-cycle process is discussed in two recently issued quarterly reports.[53,54]

Gaseous Low-Decontamination Process for Uranium Dioxide Fuels

Atomics International[55,56] has reported further work on the AIROX process, in which uranium dioxide fuel is removed from the cladding and pulverized by alternate oxidation with air or oxygen at 200 to 600°C and reduction with hydrogen at 600°C. The resulting uranium dioxide powder is reenriched by blending and is then refabricated by cold pressing and sintering.

Uranium dioxide fuel was irradiated in a first cycle to burnups of 5700 to 21,000 Mwd/metric ton of uranium, processed by the AIROX procedure, then reirradiated to an additional 10,000 Mwd/metric ton of uranium in a second cycle. Postirradiation studies were conducted on this material and on irradiated uranium dioxide containing added fission-product oxides equivalent to a burnup of 100,000 Mwd/metric ton. Decladding, processing, and refabrication tests are being made with these materials. On completion of these multicycle processing studies, all fuel-processing work at Atomics International is being phased out.[56]

Carbide-Fuel Processing

Some additional information on the CARBOX process for uranium carbide fuels has been reported by Atomics International.[55–57] In the CARBOX process uranium monocarbide fuel is oxidized by air, oxygen, or steam to form U_3O_8, which is then reacted with carbon at about 1500°C (carbothermic reduction step) to regenerate the uranium carbide.

In scale-up studies of the oxidation procedure,[55,56] a total of about 100 kg of uranium monocarbide has been oxidized successfully in 3- to 10-kg batches. Air was used as the oxidant in a rotary-kiln furnace. The oxidation rates approached 2.5 kg of carbide per hour, with nearly complete utilization of the oxygen in the air. An infrared carbon dioxide analyzer in the off-gas system proved to be an excellent means of monitoring the extent of reaction. With "aged" (chemically reactive) hyperstoichiometric (carbon-rich) uranium monocarbide, over 98% of the product was −200 mesh U_3O_8. The product contained about 0.04% carbon in the form of carbonate. With unactivated hypostoichiometric material, difficulty was encountered in obtaining complete oxidations. With a feed of radioactive uranium monocarbide, the oxidation equipment operated satisfactorily and the U_3O_8 product obtained was suitable for reconversion to stoichiometric uranium monocarbide.

In the carbothermic reduction of U_3O_8 to regenerate uranium monocarbide, a two-step procedure has been investigated: (1) reduction of U_3O_8 by carbon at temperatures up to 900°C

to form uranium dioxide and (2) conversion of the uranium dioxide to uranium monocarbide by reaction with carbon at higher temperatures (up to about 2000°C). The use of carbon instead of hydrogen for the reduction of U_3O_8 to uranium dioxide eliminates an undesirable reaction and produces a reactive product. Several carbothermic reduction experiments[55] have been performed with U_3O_8 charges as large as 20 kg. Some difficulty was encountered in attempting to produce a hypostoichiometric product, but it is possible to produce hyperstoichiometric uranium monocarbide of the desired carbon content.

Some time ago a cost study was published[58,59] comparing the AIROX process and aqueous processing in a uranium dioxide fuel cycle. A similar study has been carried out recently on the use of the CARBOX process in a uranium monocarbide fuel cycle.[57] The study was based on a single 360-Mw(e) sodium-cooled thermal power reactor and on a complex of three reactors having a total power of 1000 Mw(e). Closed-cycle on-site processing was assumed. Because of the partial recycle of fission products from the CARBOX process, an additional ^{235}U burnup of about 4.3% would be required over nine cycles (~14.5 years) as compared with the ^{235}U required in the absence of recycled fission products. Although the inventory and burnup requirements would be greater for the CARBOX process then for aqueous processing, the additional cost from these sources is more than offset by savings incurred in other parts of the on-site closed fuel cycle. A potential net saving of about 0.2 mill/kw-hr is indicated. For a fast reactor system, considerably larger savings should be possible through reduced inventory and processing charges, and because the burnup penalty resulting from recycle of fission products would be much less in a fast-neutron spectrum. (R. K. Steunenberg)

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Section

IV

Reactor Fuel Processing

Waste Disposal

Treatment of Low- and Intermediate-Level Wastes by Incorporation in Asphalt

Incorporation of low- and intermediate-level-activity wastes in asphalt offers a promising disposal method. Asphalt has a relatively low melting point, is insoluble in water, and has very good adhesive or coating properties. The method appears to be simple, safe, and inexpensive for the storage of wastes whose radioactivity level is low enough so that heat generation is not a problem but whose radioactivity level is high enough so that discharge to the environment is not possible. The asphalt method of disposal seems to be relatively insensitive to the type of material being coated and, within limits, appears to be independent of local geologic and hydrologic conditions. The product is easily shipped to a burial ground in a controlled area.

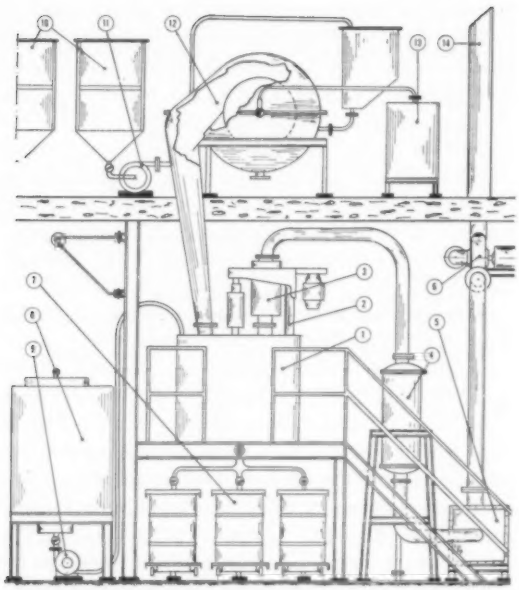
The idea for this method originated at Mol, Belgium.[1,2] Research on this method is also being carried out at the Marcoule Center in France[3] and at the Oak Ridge National Laboratory (ORNL).[4,5] At Mol,[1,2] various radioactive wastes, such as incinerator ashes, sludges from the flocculation treatment of aqueous wastes, and concentrated aqueous solutions from evaporators, have been dispersed in asphalt.* The concentrate is gradually injected into hot asphalt (200 to 230°C), during which time vigorous agitation of the mixture is taking place. The energetic mixing makes it possible to use this method for treating concentrates in which the water content ranges up to 99%. The water evaporates very quickly while the dehydrated waste is being dispersed in the asphalt. The resulting mixture is homogeneous and, after cooling, is a solid, almost nonleachable mass. Up to 45% dry solids may be incorporated in the mixture.

On the basis of the results of laboratory-scale and pilot-plant tests, an installation (see Fig. IV-1) having an evaporative capacity of 100 liters/hr has been constructed. The installation will be used principally for the processing of sludges with high water contents that result from the chemical treatment of radioactive wastes. Operation of the installation is as follows. Asphalt is pumped from a preheating tank (8) into an electrically heated (90 kw) mixing tank (1). The sludge is proportionally fed from a drum filter (12). Mixing and dispersion are accomplished with a high-efficiency mixer (2) that is fitted with adjustable blades and is driven by a 10-hp motor. The asphalt-sludge mixture is poured into a storage container (200-liter drum). Decontamination of the off-gas is accomplished by passing the off-gas first through a condenser and then through an electrostatic type filter.

Static leaching tests at 15°C using distilled water and seawater were carried out on radioactive samples of asphalt-waste concentrate mixtures. Leach rates were measured for about one year and were as follows:

Sample mixture ratio		Leach rate, 10^{-4} g/(cm²)(day)	
Asphalt	Concentrate	Distilled water	Seawater
4	6 (sludge)	1.1–2.0	0.7–1.2
4	6 (incinerator ash)	2.0	1.3
4	8 (evaporator)	4.0	2.7

*Asphalts (Mexphalt series) with melting points above 150°C which are produced by the Shell Company were used in these tests. With these asphalts the resulting mixtures are not too fluid at ambient temperatures.



1. Mixing tank
2. Mixer
3. Separator
4. Condenser
5. Electrostatic filter
6. Ventilator
7. Mixture outlet
8. Preheating of asphalt
9. Asphalt feed pump
10. Sludge freezing
11. Sludge pump
12. Drum filter
13. Filtrate
14. Gases outlet

Fig. IV-1 Schematic drawing of the industrial processing plant at Mol, Belgium, for incorporating sludges in asphalt.[2]

Irradiation of several samples to 10^8 rads produced no change in the leach rate and no significant physical deterioration.

Storage of drums of asphalt concentrate is being evaluated at Mol. Migration rates of various radionuclides in the sandy soil of this site were determined. On the basis of this study and assuming a yearly average production of 400 drums of the asphalt-concentrate mixture, calculations showed that the following maximum amounts of various activities could be accumulated per year at the Mol storage site:

Activity	Total curies/year
Alpha emitters	10
Long-lived gamma emitters	
^{137}Cs	500
^{147}Pm	200
^{106}Ru	100
Miscellaneous, $t_{1/2}$ = 1 year	200

A steady-state leach rate would be reached after 100 years of accumulation of asphalt-treated wastes. This takes into account the diffusion velocity of active materials in the mass of radioactive asphalt and the half-life of the considered nuclide. Under steady-state conditions the following quantities would be eluted annually:

Radionuclide	Millicuries/year
^{137}Cs	75
^{90}Sr	75
^{106}Ru	2.2
^{147}Pm	7.0

These quantities represent the most pessimistic case. In actual practice, however, the asphalt blocks will not be stored in a water table. Additionally they can be easily protected against rainwater percolation.

In migration by water-table transport of the eluted activity, only the strontium and cesium need be considered. However, cesium is efficiently retained by the soil and poses no special problem. Strontium, however, has a high relative migration velocity in groundwater, and this constitutes the limiting factor in the storage capacity of the site.

At the Marcoule Center, workers[3] have investigated the asphalt treatment of sludges that result from the chemical treatment of medium-level-activity (10^{-3} to 1 curie/m^3) and high-level-activity (1 to 25 curies/m^3) plant aqueous wastes. The resulting sludges have a high water content (from 75 to 83%). A process has been developed and successfully tested. In the process, surface-tension agents are used which cause the water to exude from the sludge. The surface-tension agent is first added to the sludge, after which hot (60°C) asphalt is poured into the sludge. After a brief mixing period, the major portion (82 to 89%) of the sludge water is exuded and is then separated from the coated sludge. The small amount of residual water remaining in the coated sludge is boiled off. The asphalt-sludge mixture is then heated to 130°C, at which time it is poured into storage containers. Significant reductions in the volume and weight of sludge to be stored are achieved with this process. The activity level of the water that is exuded from the medium-level-activity and high-level-activity sludges is only slightly higher than the effluents produced in the

original chemical treatment of the two plant wastes. The medium-level-activity effluents do not generally require further treatment before being discharged; the high-level-activity effluents are sent to the medium-activity-level plant for further processing.

In the ORNL studies,[4,5] emulsified asphalt* is being used. Preliminary experiments were carried out with simulated ORNL waste-evaporator concentrate† which would be produced in the processing of intermediate-level-activity aqueous wastes. The simulated waste concentrate was readily incorporated into the emulsified asphalt by mixing at 550 rpm, heating the mixture at 130°C, holding at this temperature until all the water had been evaporated, and then pouring the mixture into a container. Figure IV-2 is a photograph of an asphalt-concentrate product. Volume reduction factors (ratio of volume of waste solution to volume of asphalt product) of 2 were obtained. Dynamic leaching tests were carried out in distilled water at 25°C with an asphalt product produced from simulated ORNL evaporator concentrate containing added ^{137}Cs, ^{106}Ru, and ^{85}Sr. The solids content of the asphalt product amounted to 62 wt.%. At the end of 10 weeks, the cesium and ruthenium leach rates were 2×10^{-4} and 6×10^{-7} g/(cm^2)(day), respectively, and no detectable amounts of strontium had leached from the asphalt product. The sodium leach rate for this 10-week period amounted to 3×10^{-4} g/(cm^2)(day). These leach rates are higher than those reported at Mol for asphalt-matrix products containing 20 wt.% solids from evaporator concentrates. On the basis of the ORNL work, it is believed that the leach rate is affected by the percentage of incorporated solids and by the species being leached[4] (Cs and Na > Ru and Sr).

Fig. IV-2 Asphalt product incorporating simulated intermediate-level-activity waste solution. The product represents a volume reduction of 2 and contains 62 wt.% solids from the waste solution.[5]

Table IV-1 ABSORBED DOSE* OF ASPHALT-MATRIX PRODUCTS† INCORPORATING RADIOACTIVE SOLIDS FROM INTERMEDIATE-LEVEL-ACTIVITY WASTES[4]

Elapsed time, years	1	10	100	1000
^{137}Cs,‡ curies/gal of waste				
0.1	2.6×10^5	2.3×10^6	1.1×10^7	1.3×10^7
5	1.3×10^7	1.2×10^8	5.5×10^8	6.2×10^8
^{106}Ru,§ curies/gal of waste				
0.1	3.1×10^5	6.2×10^5	6.2×10^5	6.2×10^5
5	1.6×10^6	3.1×10^6	3.1×10^6	3.1×10^6

*Assuming infinite homogeneous medium.

†Asphalt-matrix product represents a volume reduction of 2 from the waste and has a density of 1.5 g/cm^3.

‡Energy of disintegration, 0.8 Mev; decay constant, 2.1×10^{-2} year^{-1}.

§Energy of disintegration, 1.3 Mev; decay constant, 6.9×10^{-1} year^{-1}.

Possible disadvantages of an asphalt matrix may be its relatively low melting temperature and stability toward radiation. However, workers at ORNL had previously shown that, in general, asphalts (and tars) can be used successfully in radiation environments so long as the total radiation dosage does not exceed 10^9 rads, although these materials may increase from 12 to 30% in volume under such doses of radiation.[6] Conservative calculations[4] (Table IV-1) show that these doses will not be exceeded for most intermediate-level-activity wastes.

Conversion of High-Level-Activity Wastes to Solids

Hanford Demonstration of Waste-Solidification Prototypes

At Hanford the phosphate-glass [Brookhaven National Laboratory (BNL)] pot-calcination

*The asphalt emulsion used in these studies is defined in Federal Specification SS-A-674b (Emulsion Paving Asphalt) as type RS-2, a rapid-settling high-viscosity emulsified asphalt for surface treatment. The material used contained 35 wt.% H_2O.

†Molar composition of waste: 6.61 Na^+, 0.19 NH_4^+, 0.22 Al^{3+}, 0.35 SO_4^{2-}, 0.056 Cl^-, 2.06 OH^-, and 4.64 NO_3^-.

(ORNL), and radiant-heat spray-calcincation (Hanford) processes are scheduled for pilot-plant demonstration during 1965 with actual high-level-activity liquid wastes.[7] Information needed for the design, development, and operation of prototype equipment is being obtained in a cooperative program in which BNL, ORNL, and Hanford are participating.

Following the remote installation of in-cell equipment[8–11] (see Fig. IV-3) for the demonstration of the phosphate-glass process (Hot-Cell Glass Experiment), two runs[11] with Purex-based waste were made. The process flow sheet used in these runs is shown in Fig. IV-4. Two operational schemes are indicated. Scheme 1 is being used during the initial runs to ensure radiologically safe operation. It differs from scheme 2 in that refluxing sulfuric acid vapors are employed for trapping the off-gas fog from the melter. As a result, scheme 1 has not yielded as much data on off-gas behavior as will scheme 2.

Iron and phosphoric acid were added to the simulated and actual plant-level-activity Purex 1WW wastes used in the runs. The iron (Fe^{3+}) content was increased from about 0.3*M* to about 0.5*M* in order to decrease leachability and to yield a more stable glass. Sufficient phosphoric acid (274 ml per liter of waste solution) was

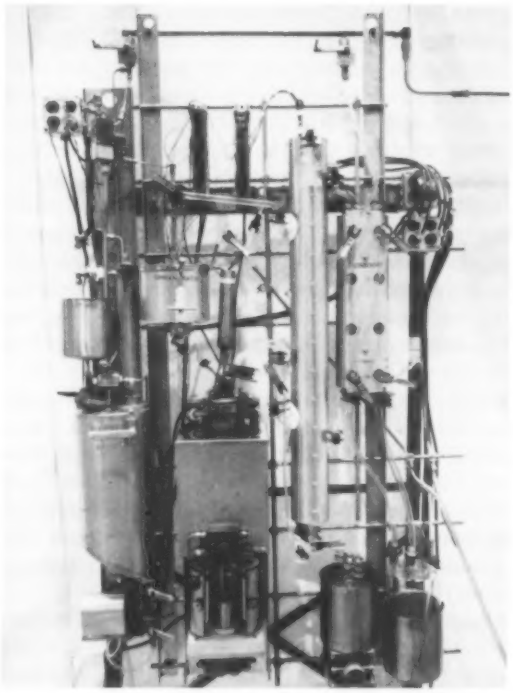


Fig. IV-3 Apparatus for Hot-Cell Glass Experiment at Hanford[11] (scheme 1).

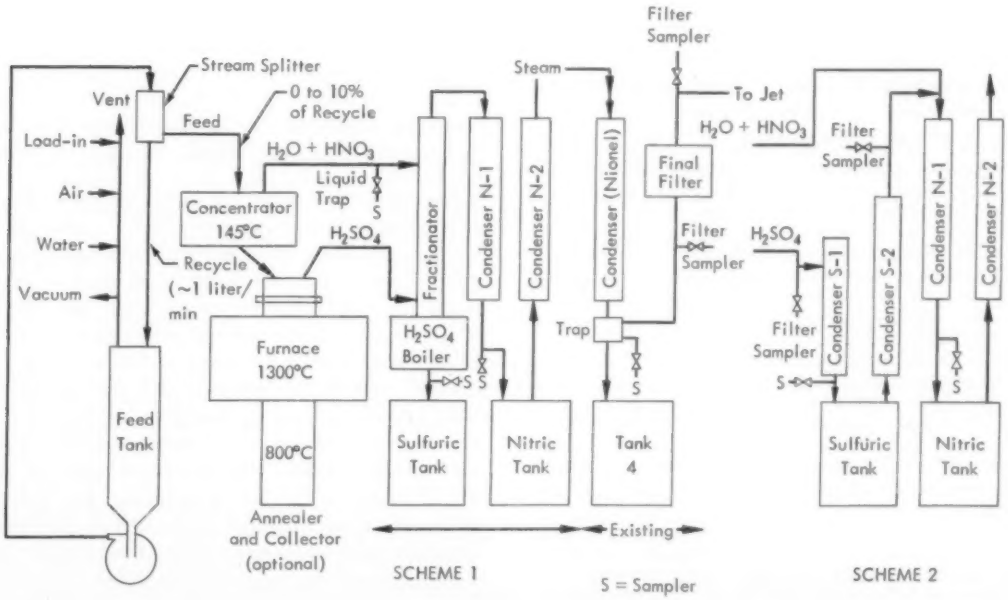


Fig. IV-4 Flow sheet for Hot-Cell Glass Experiment.[11]

added to yield a ratio of metallic ion, M^+, to phosphorus of 0.93.*

In the first run (H-1), treated simulated feed was used for the initial one-third of the run and treated actual plant waste was used for the reaminder of the run. The run was completed despite a number of operational and equipment difficulties that occurred. A nonglass solid product was formed.† The product volume amounted to about 0.5 liter, which is equivalent to a volume reduction of about 11-fold when based on the treated volume (5.6 liters) of feed used and about 9 when based on the untreated volume (4.4 liters) of feed used.

For the second run (H-2), equipment deficiencies were corrected. The run was completed satisfactorily; no operational or equipment difficulties were encountered. The treated feed consisted entirely of actual plant-level-activity waste. An excellent glass product was obtained in this run, and its color was a typical glossy black (Fig. IV-5). Polished sections of the product were examined and found to be homogeneous and without structure. The product volume amounted to about 0.3 liter, and this represents a volume reduction of about 10-fold when based on the untreated volume (3 liters) of feed used. The total activity in the product corresponds to about 600 curies/liter (2.5 watts/liter).‡

In run H-2, over 99.8% of the fission products charged were retained by the liquid in the concentrator. Also, unexpectedly, all the fission products, except for about 0.7% of the ruthenium originally charged, was retained by the glass product; most of the unretained ruthenium was trapped by the fractionator. Overall decontamination factors of greater than 10^8, and in some instances greater than 10^9, were achieved during this run.

Fig. IV-5 Glass product formed in Hanford demonstration of BNL phosphate-glass process. Hot-Cell Glass Experiment run H-2 (Ref. 11).

Hanford Radiant-Spray Calciner–Continuous Powder-Melter Studies

Hanford is continuing the development of radiant-heat spray calcination[11,12] (Fig. IV-6) for the treatment of high-level-activity aqueous wastes from the Purex process. In this technique the feed solution is sprayed into the top of a heated column that is maintained at about 800°C. The spray droplets are converted to a powder that falls into a heated pot where the calcination process is completed. Either a sinter or melt results, depending on the composition of the residue. A continuous melter is also being developed[11] for converting the powder from the spray calciner to a melt or phosphate "glass" product which is intermittently discharged to a final storage container.

Semiworks tests of a 14-in.-diameter radiant-spray calciner with an installed 10-in.-diameter

*Barton[11] at Hanford has shown that devitrification of the product glass occurs rather quickly unless the M^+-to-P ratio is within ±5% of 1.00. Since some P_2O_5 loss occurs in the melter, and a slight excess of phosphoric acid improves solubility in the concentrator, an initial M^+-to-P ratio of about 0.93 appears optimum. This characteristic is not evident with air-quenched glass from a continuous melter. However, it is quite significant under the relatively slow cooling conditions that are encountered with a melt retained in the furnace during cooldown.

†During the course of the run, it was necessary to add phosphoric acid to the concentrator to clean it up when it became plugged. Because of the additional phosphoric acid, the product had a high phosphorus content (M^+-to-P ratio of about 0.67), which may account for its not having formed a true glass or its having devitrified on cooling.

‡The low activity in the Purex 1WW waste used is due to aging and to the loss of considerable amounts of zirconium-niobium and cerium to a sludge which precipitated on storage and which was incompletely redispersed prior to withdrawal from the storage cask.

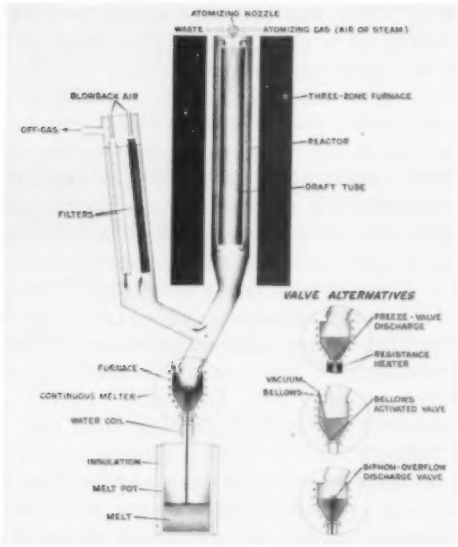


Fig. IV-6 Engineering-scale spray calciner and continuous melter.[13]

draft tube* were carried out. For atomizing the feeds an external-mix type nozzle† was used. The tests used nonradioactive feeds consisting of sulfate-bearing Purex-based waste solutions (80 gal per ton of uranium) to which were added glass-forming agents. Either colemanite (nominal composition, $Ca_2B_6O_{11} \cdot 5H_2O$; Tyler mesh size, < 300) or borax ($Na_2B_4O_7 \cdot 10H_2O$) was used as a glass former in feeds whose sulfate content amounted to 0.14*M* and whose free nitric acid concentration was varied between about 0.2*M* and 5*M*. In runs with feeds containing added colemanite (174 g/liter) and free nitric acid concentrations up to 5*M*, operation of the calciner was quite satisfactory, and no troublesome amounts of calcine were deposited on the calciner wall. The acidity of the feed seemed to affect only the ease with which the solid colemanite could be slurried. In high-acid feeds the colemanite was more easily dispersed, and fewer agglomerates were present than in the low-acid feeds. In low-acid feeds the suspended agglomerates produced partial pluggging of the feed control valve. In runs with feeds containing added borax (85 g/liter), a meltable calcine was formed which did not melt or sinter on the calciner wall at 650°C.‡

In other semiworks studies,[11] tests of the continuous melt step were carried out in which the solid glass former was added to the melt pot for mixing with the radiant-spray calcine instead of adding the glass former to the spray-calciner feed. The calcines used were produced from nonsulfate type Purex-based waste solutions. Sodium orthophosphate ($NaH_2PO_4 \cdot H_2O$) and borax glass frit were used as flux additives. Adequate mixing of calcine and flux in the melt pot was achieved without the use of mechanical means of agitation.

When solid sodium orthophosphate and calcine were simultaneously added to the melt pot at 1000°C in the weight ratio of 2.42 parts sodium orthophosphate to 1 part calcine, a phosphate-glass product was formed without difficulty. However, the melt that formed was corrosive to the melt pot which was fabricated of type 310 stainless steel. When borax-glass frit and calcine were added in weight ratios of 1.61 or 1.89 parts of frit to 1 part of calcine and melted at 900 to 950°C, excessive foaming occurred.

Semiworks tests[11] were also carried out in which the 14-in.-diameter radiant-spray calciner and the melt pot were operated as a composite unit. Except as noted below, the calciner was operated without a draft tube. The feeds consisted of nonradioactive Purex-based waste solutions to which was added borax-glass frit or colemanite. Four runs of varying duration (3 to 50 hr) were made.

One run (3 hr) was made with a feed (80 gal per ton of uranium) containing added borax-glass frit (85 g/liter). The temperature of the calciner was maintained at 650°C, and that of the melt pot wall, between 950 and 1000°C. The spray calciner operated satisfactorily, and there was no evidence of calcine sintering. In the melt pot the calcined solids melted readily at 850 to

*A draft tube serves to improve reactor performance by increasing heat transfer at a given calciner wall temperature and by reducing wall deposits by better control of gas currents within the calciner. The draft tube is a hollow cylinder mounted concentrically within the calciner and has openings at its upper and lower extremities to permit recirculation of gases from the bottom of the calciner up past the heated calciner walls and back down through the spray-filled central area of the reactor.

†A No. 5 external-mix nozzle, product of Spraying Systems Company, Bellwood, Ill. The diameter of the atomizing gas orifice was increased to $^7/_{32}$ in.

‡In earlier work[10] with Redox-based feeds containing added borax (250 g/liter), heavy deposits of partially melted powder formed on the calciner wall at 600°C.

950°C and formed a nonglassy product. The melt was primarily dark brown in color, but it also contained a small amount of a yellow second phase that has not yet been identified.

The other three runs (5, 40, and 50 hr) were made with feeds (160 gal per ton of uranium) containing added colemanite (86.7 g/liter). The wall temperature of the calciner was maintained between 650 and 700°C, and that of the melt pot, between 950 and 1000°C. The melt temperatures ranged from 850 to 950°C. The level of the melt was successfully monitored by means of a conductivity probe. In the portions of the long-duration runs that were made with a 10-in.-diameter draft tube installed in the calciner, calcine deposits formed on the draft tube. This buildup of calcine on the draft tube was not detected in runs of relatively short duration (3 to 5 hr). When no draft tube was used, there was no adverse accumulation of calcine on the calciner wall. In the 50-hr run, localized corrosion produced a hole in the wall of the melt pot (type 310 stainless steel) after 40 hr. The corrosion may have been accelerated because the melt was being inadvertently sparged with air. Air was introduced into the system through the discharge valve whenever the system pressure fluctuated.

Hanford Study of Transient Thermal Behavior in Calcined or Glass-Fixed Wastes

The transient thermal behavior of calcined high-level-activity wastes is being studied at Hanford.[9–11] This study was undertaken to determine the parameters affecting the size of a container for final storage of a high-level-activity waste that has been either calcined or converted to a glassy solid. The study shows that the maximum size of a container may be limited by the transient conditions existing during the period that follows the fixation and stabilization of the waste rather than by the equilibrium conditions existing during storage. Thus the temperature reached during this transient period may be higher than that (steady-state temperature) reached during storage. On the basis of the work of Olcer and Miller,[14] dimensionless correlations and curves have been developed for the maximum temperatures achieved in cylinders[9,10] and annular containers[11] with internal heating. For cylinders,[10] curves are given which relate the heat-generation rate and the Nusselt number to the maximum centerline temperature reached and the time to reach the maximum centerline temperature. For annular containers, curves are presented which relate the heat-generation rate and the inner-to-outer radius ratios with an insulated inner wall[11] to the maximum temperature reached.

A heat-transfer study[4] was also made at Hanford which is related to the Hanford demonstration of the ORNL pot-calcination process.[15] The furnace for the demonstration of this process inductively heats a susceptor that surrounds the calcination pot.[4] Heat will be transferred from the susceptor operating at 1000 to 1100°C to the pot wall (900°C) by radiation. The induction coils are water cooled and are protected by a layer of insulation to prevent high heat loss. The maximum centerline temperatures were calculated for an 8-in.-diameter pot while it was cooling in the induction furnace. The temperatures were determined for various operating conditions and are shown in Table IV-2.

Table IV-2 MAXIMUM CENTERLINE TEMPERATURES FOR COOLING OF 8-IN.-DIAMETER POTS IN AN INDUCTION FURNACE[4]

Conditions	Average heat-transfer coefficient outside of pot*	Maximum pot centerline temperature of calcine,† °F	Maximum pot centerline temperature of glassy solids,‡ °F
1.5-in. insulation§ and susceptor	0.83	1922	1697
0.75-in. insulation§ and susceptor	1.49	1853	1685
0.75-in. insulation;§ no susceptor	1.70	1844	1684
1.5-in. insulation§ and susceptor;* 155 cfm cooling air	2.13	1831	1682
0.75-in. insulation and susceptor;* 155 cfm cooling air	2.44	1825	1682
1.5-in. insulation; no susceptor	0.87	1918	1698

*Values of heat-transfer coefficient are in Btu/(hr)(°F)(sq ft of area on pot-calciner wall).

†Fission-product heat-generation rate (Q) is 5000 Btu/(hr)(cu ft); thermal conductivity (K) is 0.2 Btu/(hr)(ft)(°F).

‡Fission-product heat-generation rate is 5000 Btu/(hr)(cu ft); thermal conductivity is 1.0 Btu/(hr)(ft)(°F).

§Fiberfrax insulation, product of The Carborundum Company.

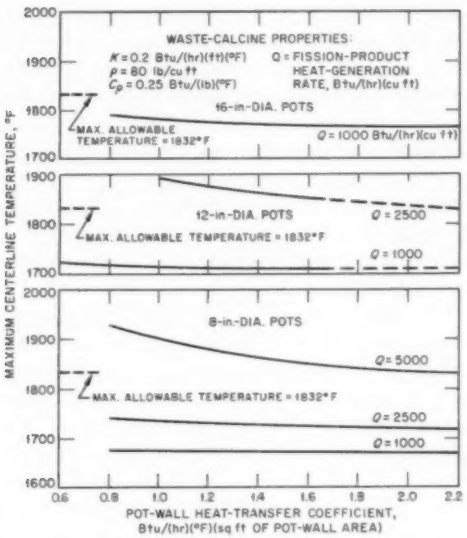


Fig. IV-7 Maximum centerline temperatures for calcine during cooling cycle.[4]

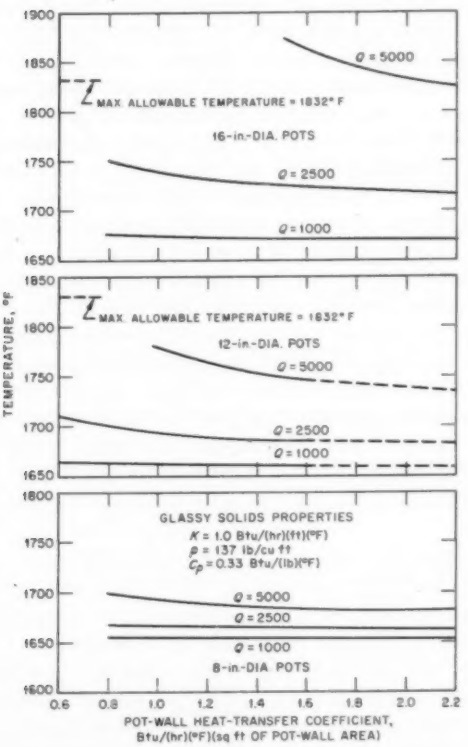


Fig. IV-8 Maximum centerline temperatures for glassy solids during cooling cycle.[4]

Maximum centerline temperatures have also been calculated for 8-, 12-, and 16-in.-diameter pots filled with calcined solids (Fig. IV-7) and glassy solids (Fig. IV-8). These transient-state cooling-rate calculations are for pots filled with solids initially at 900°C. Figure IV-7 shows that calcine internal generation rates should be limited to 5000 Btu/(hr)(cu ft) for 8-in.-diameter pots and 2500 Btu/(hr)(cu ft) for 12-in.-diameter pots. This limitation is based on a maximum allowable calcine temperature of 1000°C (1832°F). Cooling air between the pot and insulation will be needed to achieve a heat-transfer coefficient for the pot wall of at least 2.0 Btu/(hr)(°F)(sq ft of pot-wall area). Figure IV-8 indicates that glassy solids having heat-generation rates of 5000 Btu/(hr)(cu ft) can be cooled easily in 8- or 12-in.-diameter pots, even at low heat-transfer coefficients for the pot wall.

Recovery of Fission Products

As part of the Hanford Waste Management Program, ion-exchange processes using synthetic ion exchangers (zeolites) are being studied for the removal (and storage) of ^{137}Cs from the alkaline supernatant solutions of the high-level-activity Purex wastes. The technology of the process has been established in laboratory studies.[16–21] The process for ^{137}Cs removal involves carrying out a low-temperature adsorption of cesium, selective washing of the bed, and high-temperature elution of cesium with ammonium carbonate solution. The eluted cesium is concentrated, and the ammonium carbonate is recovered for reuse by distillation. The cesium-loading step of the process has been successfully tested in the plant with plant-level-activity wastes.[22]

In other laboratory work[23] a model was developed from which the breakthrough history of a tracer concentration solution may be estimated to within 10% over a wide range of operating parameters. The model has been used to predict cesium breakthrough for the plant-sized ion-exchange column at the design operating parameters. The results indicate that it may be possible to reduce the design volume of the column and the ion exchanger by 20 to 30%.

Work has also been conducted on a method that utilizes multiple crystallizations for purifying recovered cesium contaminated with so-

dium.[11] Tests were carried out with simulated cesium-product solutions containing 0.64*M* sodium and 0.08*M* cesium. A 100% excess of aluminum ammonium sulfate was added to the cesium-product solution, forming aluminum cesium sulfate. The aluminum cesium sulfate was then crystallized from the resulting solution at 5°C. After the supernatant solution was decanted, the aluminum cesium sulfate was dissolved in hot water and recrystallized from solution at 5°C. The dissolution and crystallization steps were repeated. The three crystallizations resulted in about 99.8% of the sodium being separated from the cesium.* Cesium recovery amounted to 90%. The residual cesium in the supernatant solutions from the decantation steps can also be recovered (for recycle) by this crystallization method.

Other Hanford reports on fission-product recovery have recently become available. Moore[22] has briefly summarized the work on fission-product recovery conducted at Hanford during 1953 to 1964. In work related to the recovery and purification of megacurie quantities of ^{90}Sr (Ref. 21), Richardson[25] reports the results of pilot-plant studies on the application of D2EHPA (di-2-ethylhexyl phosphoric acid) to the solvent extraction of strontium, cerium, and rare earths. Bray and Roberts[26] describe a process for the separation of cerium from promethium and other rare-earth products. The process employs oxidation of the cerium with silver-catalyzed persulfate and solvent extraction with D2EHPA.

Other Literature

In the processing of molybdenum-alloy reactor fuels, nitric acid (~3*M*) wastes containing high concentrations of stable molybdenum are produced. If these wastes can first be concentrated, the volume to be stored can be significantly reduced. Because molybdenum is present in high concentrations and its solubility in nitric acid is limited, it is desirable to remove the molybdenum before the concentration step. Jenkins and Wain[27] at Harwell have investigated a solvent-extraction method that utilizes alkyl phosphoric acids for removing the molybdenum. The molybdenum was successfully extracted from synthetic waste solutions (~2.6*M* HNO_3) containing added fission-product tracer elements. The extraction was achieved with either monododecyl phosphoric acid or monoheptadecyl phosphoric acid, each dissolved in kerosene. Zirconium and niobium are extracted along with the molybdenum; the selective separation of molybdenum from the zirconium and niobium in the organic phase is accomplished by back extraction of the molybdenum into an aqueous mixture of ammonium fluoride and nitric acid.

Platt and Cooley[28] at Hanford have briefly summarized the principal research and development work conducted at Hanford on the treatment of radioactive liquid wastes. Their report covers the period through the end of 1964. They have reported on the waste-solidification processes for the fixation of high-level-activity wastes and on ion-exchange processes for the treatment of intermediate-level-activity wastes.

Tharin[29] has described the storage facilities used for the spent solvent from the separations processes at Savannah River and the design and development of equipment for the disposal (by burning) of the spent solvent. Of the 290,000 gal of spent solvent sent to the storage facility (162,000-gal capacity) between mid-1955 and February 1964, some 170,000 gal have been burned. The solvent is burned by adding it slowly to a fire in a large open pan. Although large quantities of black smoke are created, the release of radionuclides to the atmosphere is negligible. Concentrations of uranium or plutonium above their limits of detection are not normally found in the smoke. Improvements in burning methods continue to be explored in order to reduce the quantity of smoke created. More than 99.9% of the main contamination, ^{106}Ru, remains in the residue. The residue, which is relatively insoluble in water, is buried, as are the used burning pans, in soil. The soil layer is sometimes covered with a layer of bentonite[30] which forms a barrier to water seepage.

Emelity, Christenson, and Fowler[31] at Los Alamos have reported on the development of a fixation method for the disposal of a 6*M* to 7*M* nitric acid waste containing approximately 1 mg of ^{239}Pu per liter and 0.1 to 1 mg of ^{241}Am per liter. The method consists of the following steps: (1) neutralizing the acid waste with 50% sodium hydroxide solution and (2) adding the neutralized waste (6⅔ gal per bag of cement) to a mixture of cement–3 wt.% vermiculite. This method pro-

*Cesium of this purity would be considered satisfactory for use in the proposed Hanford Isotopes Production Plant.[24]

duces a fixed waste which, after curing, has an extremely low leach rate. A plant for handling these wastes has been in operation since November 1959. To the middle of 1964, the plant has processed some 86,000 gal of acid wastes containing approximately 360 g of plutonium and approximately 345 g of americium. The fixed waste produced is stored in some 6100 fifty-five-gal drums. (P. Fineman)

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Section

V

Reactor Fuel Processing

Production of Uranium, Thorium, and Plutonium and Their Compounds

Production of Uranium Dioxide

Reduction of Higher Oxides

The uranium-oxygen system is highly complex. The existence of at least five thermodynamically stable uranium oxides (UO_2, U_4O_9, U_3O_7, U_3O_8, and UO_3) has been definitely proved, and several additional oxides have been reported. The system is further complicated by polymorphism, formation of solid solutions, and metastability. Thus the mechanisms governing reduction processes are not readily defined in this system. The rate of reduction reactions has been shown to be determined by the structure of the solid surface which, in turn, is modified as the reactions progress. Zhukovskii and Vlasov[1] reported the results of a study of the kinetics of the reduction of U_3O_8 with ammonia in the temperature range 500 to 650°C. At 500°C the reduction of U_3O_8 with ammonia proceeded only to the extent of 5 to 7%. At temperatures of 600°C and above, the reaction progressed rapidly. The apparent activation energy for the reduction reaction was found to be 50.5 ± 4.5 kcal/mole. An increase in pressure of ammonia resulted in an increase in the overall rate of reduction of U_3O_8. The following scheme was suggested to describe the phase transformations that accompany the reduction of U_3O_8 by ammonia:

$$U_3O_8 \xrightarrow{1} U_3O_{8-x\ max.} \xrightarrow{2} U_4O_9 \xrightarrow{3} UO_{2+x\ max.} \xrightarrow{4} UO_{2+x}$$

A marked decrease in the rate of reduction was observed for step 2. This was attributed both to the difficulty in removing the last parts of oxygen from the solid solution in the $U_3O_{8-x\ max.}$ phase and to the difficulty in forming nuclei of a new phase (U_4O_9) having a different crystal lattice. It was suggested that the reduction of U_3O_8 occurs in two parallel processes: (1) reduction by ammonia that is decomposed directly on the surface of the oxide being reduced and (2) reduction by gaseous hydrogen present in the gas phase. Since the quantity of gaseous hydrogen present throughout the reduction process is negligible, the controlling step apparently is that of reduction of the oxide by undissociated ammonia. This seems to be confirmed by the high value of the activation energy observed in these studies.

In other work Sato, Doi, and Uchikoshi[2] investigated the hydrogen reduction of U_3O_8 to UO_2 and defined the phase changes that occur on the basis of X-ray diffraction data. Cordfunke and Aling[3] measured the equilibrium pressure of oxygen in the system gamma $UO_3 + U_3O_8$ as a function of temperature, and on the basis of these measurements they established a tentative phase diagram for the $UO_3 + U_3O_8$ system. The heat of formation of gamma UO_3, derived from the oxygen-pressure measurements, was determined to be $\Delta H_{298°K} = 293.5$ kcal/mole. In a study of the effects of the presence of alkali-metal carbonates on the reduction of UO_3 by carbon monoxide, Vlasov and Shalaginov[4] observed that the presence of lithium carbonate reduces the rate of reduction, whereas additions of sodium or potassium carbonate up to 5 mole % appreciably increase the rate of reaction. It was suggested that the increase in the rate of the reduction reaction by the addition of sodium or potassium carbonate is caused by formation of alkali-metal uranites, which in turn increases the number of free electrons on the surface layer of the UO_3.

Walker[5] observed that the nature of the oxidation of UO_2 to U_3O_8 is principally affected by the surface area of starting material. In UO_2

powders of surface area greater than 2 m^2/g, oxidation was diffusion controlled up to the U_3O_7 phase, which then oxidized to U_3O_8 at temperatures above 240°C. The activation energies were in the range 20 to 27 kcal/mole. For material with very low surface area, both electrolytic UO_2 powder (0.040 m^2/g) and sintered pellets (5 cm^2/g) were oxidized by nucleation and growth processes. The growth activation energies for the two materials were 32.2 and 26.4 kcal/mole, respectively. Material with intermediate surface area gave oxidation curves that were hybrid between the other two types.

Conversion of Uranium Hexafluoride to Uranium Dioxide

A process for the direct conversion of uranium hexafluoride to uranium dioxide using fluidization techniques has been developed at Argonne National Laboratory (ANL).[6,7] Two different methods for producing spherical UO_2 particles were demonstrated: (1) a two-step method[6] in which UF_6 is converted to uranyl fluoride (UO_2F_2) by hydrolysis with steam at about 200°C followed by reduction of UO_2F_2 to UO_2 by reaction with a steam-hydrogen mixture; and (2) a one-step method[7] wherein UF_6 is reacted with a mixture of steam and hydrogen in a fluid bed of UO_2 at 650 to 700°C to produce high-density UO_2 particles suitable for use in dispersion and compacted fuel elements. A patent on the one-step method for producing dense UO_2 particles has been issued to Knudsen, Jonke, and Levitz.[8]

Process studies on the two-step method were carried out in 3-in.-diameter Monel fluid-bed reactors.[6] The equipment used for the hydrolysis of UF_6 to UO_2F_2 is shown in Fig. V-1. A column of similar design but with the filter vessel integral with the reactor was used for the batch reduction of UO_2F_2 to UO_2. Demonstration tests on the hydrolysis of UF_6 to UO_2 were conducted at 230°C, with a UF_6 feed rate of 100 g/min and a steam rate of 3.25 times the stoichiometric requirement. The starting beds consisted of 7 to 8 kg of −20 +200-mesh uranyl fluoride; the average particle diameter ranged from 301 to 368 μ. The growth of the bed particles due to deposition of the newly formed uranyl fluoride was offset by feeding seed particles (−60 +200 mesh; average particle diameter 160 μ) at a rate of 1 kg/hr during the run.

Complete conversion of the hexafluoride to uranyl fluoride was achieved in all runs. Uranium losses as determined by analysis of the off-gas condensate stream were consistently less than 0.01% of the quantity of uranium fed. The UO_2F_2 product was a high-density material (6.0 g/cm^3, equivalent to 94% of the theoretical density) with a bulk density of 3.5 g/cm^3. Nickel content was low, 6 ppm, indicating that only minor corrosion of the Monel reactor occurred at operating temperature.

Although the bulk of the UF_6 reacts on the surface of the UO_2F_2 bed particles, a small portion was found to react in the vapor phase and form very fine particles of UO_2F_2 (−325 mesh) which were elutriated into the filter vessel. The amount of fines formed appeared to be related to the average diameter of the particles in the bed, smaller amounts of fines being formed when beds of coarser particles were used. The quantity of fines collected in the filter vessel represented 1.1 to 7.4% of the hexafluoride fed to the system. During these studies the deposition of UO_2F_2 on internal surfaces at a rate of 20 μ/hr was also observed. Although the deposition rate is not large, occasional shutdown of the reactor to remove the accumulated solids might be required in long-term operation. In exploratory tests at higher temperatures (500°C), deposition of material on the reactor walls was eliminated, although

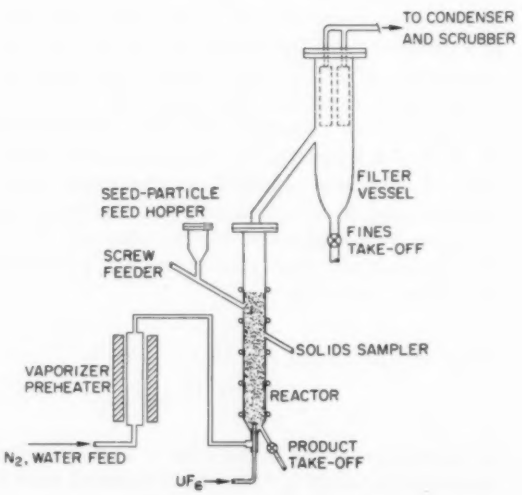

Fig. V-1 Schematic layout of equipment for fluid-bed hydrolysis of uranium hexafluoride to uranyl fluoride.[6]

greater quantities of fines were found under those conditions. The product formed in the high-temperature tests was found to be U_3O_8 rather than UO_2F_2. It was suggested that operation at a temperature between 200 and 500°C would minimize the deposition of solid materials on the walls of the reactor.

The second step of the two-step process[6] involved the fluid-bed reduction of the UO_2F_2 obtained by the hydrolysis of UF_6. The objectives of the development work were to determine the effects of operational variables and to establish conditions for preparing UO_2 powder with low fluoride content suitable for pellet fabrication. Reduction of UO_2F_2 to UO_2 was demonstrated in batch tests in a 3-in.-diameter fluid-bed reactor at temperatures of 600 and 650°C, and mixtures of steam and hydrogen were used as the fluidizing gas. The presence of steam in the reactant stream was found to enhance markedly the fluoride-removal rate; the optimum gas composition was found to be a 50:50 mixture of steam and hydrogen. With this mixture a residual fluoride content of 200 ppm was achieved in 4 hr at 650°C. The hexavalent-uranium content of the UO_2 product ranged from 1.7 to 3.9%, which is somewhat higher than expected in view of the high degree of reduction indicated by the low fluoride content of the material.

No marked effect of particle size on fluoride removal was noted. However, appreciable breakup of individual particles occurred during the reduction studies. Overall results showed an average decrease in mean particle diameter of 40 to 50 μ/hr. The presence of fine (< 200 mesh) material in the bed to the extent of 35 wt.% did not appear to affect the fluidization characteristics of the bed. The production of fine particles does not affect subsequent processing of the UO_2 since the product would be ground to a fine powder for pellet fabrication.

The UO_2 product had a bulk density of 4.5 g/cm^3 and a surface area of 0.32 m^2/g. Contaminants in the product other than fluoride were primarily nickel, 160 ppm, and copper, 40 ppm, which were introduced by corrosion of the Monel reactor. Sintering tests performed on the UO_2 product indicated that pellets having a density of 94% of theoretical can be produced by grinding the UO_2 to −325 mesh and sintering without binder at 1700°C in a hydrogen atmosphere.

A report describing the engineering development of a fluid-bed process for the preparation of dense UO_2 particles from UF_6 has been recently issued.[7] This report reviews work that has been reported in previous issues of *Reactor Fuel Processing*.[9,10] Spherical particles of UO_2 with densities up to 9.75 g/cm^3 (89% of the theoretical density) have been prepared by proper adjustment of processing parameters. In the process UF_6 is reacted with mixtures of steam and hydrogen in a bed of UO_2 fluidized by the reactant gases and maintained at 650 to 700°C. The solid-reaction-products deposit is a dense layer on the surface of the bed particles. The operating procedure involves alternating periods of UF_6 feed with periods in which only steam and hydrogen are fed to reduce the fluoride content of the UO_2 product. The product is withdrawn at the end of each cleanup period.

A characteristic of the fluid-bed process for converting UF_6 to dense oxide particles is growth of the oxide particles during the conversion period. Continuous operation of the fluid-bed reactor is thereby limited by the growth of the particles to a size that cannot be conveniently fluidized, and resizing of the oxide-bed material at prescribed intervals is required. An oxidation-reduction technique[7] for achieving *in situ* size reduction was developed as an alternative to a method involving the introduction of seed particles to the fluid bed. Particle breakup occurs as the UO_2 bed is oxidized to U_3O_8. Oxidation is carried out at 400°C using 20 vol.% air in nitrogen. Reduction of the partially oxidized material to UO_2 is achieved at 650°C using 100% hydrogen. As little as 0.25 times the stoichiometric amount of oxygen needed for complete oxidation provides the desired amount of particle breakup (average particle size reduced to one-half of the starting size).

The uranium dioxide particles in the size range −18 +140 mesh and having densities up to 9.75 g/cm^3 were produced. Uranium hexafluoride feed rates in the range of 17 to 50 g/min [30 to 88 lb of uranium/(hr)(sq ft of reactor cross section)] were evaluated in the program. The higher rates produced a material of somewhat lower density. The mole ratio of steam to UF_6 in the feed had a significant effect on the density of the UO_2 product. Ratios of about 2:1 resulted in the production of material of the highest density. The average residual fluoride content of the product after the fluoride cleanup period was approximately 250 ppm.

Densification of the UO_2 particles to about 10.5 g/cm^3 (96% of the theoretical density) and reduction of the fluoride content to about 5 ppm was achieved by sintering the oxide in hydrogen at 1700°C.

Workers at Oak Ridge National Laboratory[11–13] prepared dense crystals of UO_2 by the high-temperature reduction of UF_6 from a gas phase containing hydrogen and water or oxygen. The process involved the injection of a UF_6-containing gas stream into a zone heated to 1300°C at a pressure of 3 to 6 torrs. With a gas-phase composition of 79.1 vol.% nitrogen, 17.3 vol.% H_2O, and 3.6 vol.% UF_6 and a system pressure of 3.2 torrs, crystalline deposits of UO_2 with a density of 11.0 g/cm^3 were produced.[12] A deposit of similar density was produced at temperatures of 1250 to 1300°C from a gas phase containing 81 to 86 vol.% H_2, 9 to 12 vol.% O_2, and 4 to 7 vol.% UF_6 at a pressure below 3 torrs.[13]

Kolar, Slivnik, and Volavsek[14] described a process for the conversion of UF_6 to UO_2 based on the formation of a complex ammonium uranium fluoride by the gas-phase reduction of UF_6 with NH_3 at 40°C followed by pyrohydrolysis of the complex fluoride at 550 to 600°C. The reaction between gaseous UF_6 and NH_3 at 40°C produced a finely divided green solid with a chemical composition corresponding to $NH_4UF_5 + NH_4F$. Pyrohydrolysis of the complex fluoride with water vapor was observed to take place in two steps. The initial step involved the vaporization of NH_4F and the thermal decomposition of NH_4UF_5 to $UF_4 + NH_4F$. The pyrohydrolysis reaction took place in the second step at temperatures between 500 and 600°C. The UO_2 product was a fine material with an average particle size between 0.1 and 0.3 μ and a fluoride content of 30 ppm. Preliminary sintering tests indicated that the powder could be sintered to 94% of the theoretical density in moist nitrogen at 1350°C.

Production and Properties of Plutonium Dioxide

The role of plutonium dioxide in the production of plutonium metal or compounds for use in fast reactor fuels is that of a primary feed material. The standard feed for the production of PuO_2 or mixed $(U\text{-}Pu)O_2$ is a dilute solution of plutonium or uranium-plutonium in nitric acid. Smith and associates[15] have described the development of a process for the preparation of mixed uranium-plutonium oxides which was used as a basis for the design of a prototype fuel-element production plant. The process involves the coprecipitation of uranium and plutonium from the nitrate solution by the addition of ammonia, followed by calcination of the precipitate and reduction.

If ammonia is slowly added to the mixed nitrate solution, plutonium hydroxide and ammonium diuranate will precipitate at separate *p*H values and some heterogeneity within the precipitate will result. In the converse situation of adding nitrates to ammonia, very rapid nucleation ensures homogeneity, but the product is difficult to filter. In an attempt to produce a homogeneous, filterable material, a continuous multistage precipitation technique was developed. This technique requires a series of well-stirred precipitation stages that are interconnected by both forward and return flows (Fig. V-2). The feed solution enters at one end of the series while the precipitant (ammonia) enters at the other end, from which the product also is delivered. The forward and reverse flows are impressed by a pulse pump at the feed entrance.

Highly satisfactory precipitation has been accomplished in this unit at a *p*H of 4. The mixed precipitate settles rapidly to a bulk density of 1.5 g/cm^3 and offers very low filtration resistance.

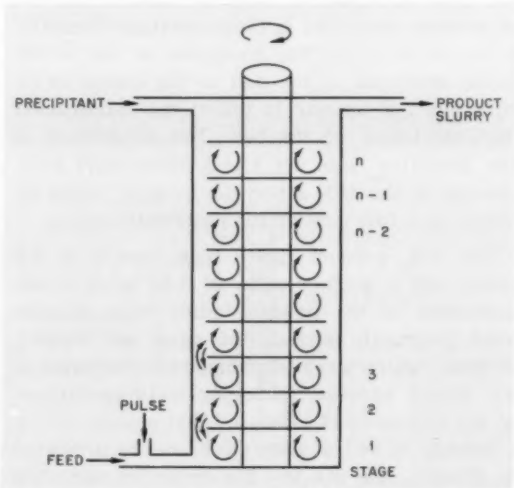

Fig. V-2 Multistage feedback precipitation unit.[15]

Conversion of the filter cake to an oxide acceptable for subsequent fabrication is accomplished in three steps, namely: drying, calcination, and reduction. Two routes were successful in achieving single-phase material with the required surface area: (1) drying and calcination in air at 250°C followed by reduction at 1000 to 1200°C in hydrogen or (2) drying and calcination in carbon dioxide at 700 to 950°C followed by reduction in dilute hydrogen in the same temperature range. The product from this process comprises a single-phase solid solution of $(U\text{-}Pu)O_2$ with an oxygen-to-metal ratio of 1.97:1 to 2.03:1. The product has a surface area of about 5 m^2/g and has been found to be most satisfactory for the preparation of high-density bodies by sintering at 1500 to 1600°C in dilute hydrogen.

In a study of the sintering behavior of PuO_2, Potter[16] observed that the temperature at which the PuO_2 was previously calcined affected markedly the final sintered density of the oxide. Oxides calcined at temperatures less than 700°C gave the highest sintered densities irrespective of the sintering temperatures or atmosphere in comparison to oxides calcined at temperatures above 700°C. In general, sintering of PuO_2 in wet hydrogen at 1500°C resulted in the highest densification of the pellets.

In the preparation of PuO_2 fuel material, knowledge of the physical and thermodynamic properties of PuO_2 is of practical importance. Thermodynamic data have been obtained for the plutonium oxide system within the composition range $PuO_{1.5}$ to PuO_2 at temperatures between 700 and 1140°C using a high-temperature galvanic cell.[17] The plutonium-oxygen phase diagram has been described by Gardner, Markin, and Street[18] and by Chikalla, McNeilly, and Skavdahl.[19] In other work Pardue and Keller[20] have measured the vapor pressure of PuO_2 in air, argon, and oxygen atmospheres in the temperature range 1450 to 1775°C. Indications were obtained that PuO_2, in addition to vaporizing congruently, can vaporize as a suboxide species in neutral atmospheres.

Preparation of Plutonium Carbides

Brown and associates[21,22] investigated a method for preparing PuC and mixed (U-Pu)C based on the reaction of hydrocarbon gases with finely divided metal. Reactive plutonium metal was prepared by hydriding billets of plutonium in hydrogen at 25°C and grinding the hydride product to a fine powder. The carbonization reaction was carried out by flowing propane gas over the hydride powder at a temperature of 600 to 800°C. The primary carbide species formed in all experiments, as determined by X-ray diffraction, was Pu_2C_3. During sintering of pellets prepared from this material, it was observed that the Pu_2C_3 phase reacts with uncarburized plutonium hydride to give amounts of PuC that depend on the original carbon content. It has been possible to produce pellets of single-phase PuC at densities greater than 90% of theoretical by sintering powders containing Pu_2C_3 and PuH_2 with the correct overall plutonium-to-carbon ratio.

Several papers[23a–c] on the preparation of uranium-plutonium carbides by the reduction of the mixed oxides with carbon were presented at the Symposium on Carbides in the Nuclear Energy Field held at Harwell in 1963. In general, the preparation procedure involves blending the mixed oxides with a calculated amount of carbon (11.5 to 12 wt.% of the oxide), pressing the mixture into pellets, and heating the pellets for 3 to 5 hr in vacuum at 1450 to 1600°C. Complete reduction to stoichiometric carbide can be achieved by providing accurate control of the carbon, good homogeneity in the feed material, and efficient removal of the CO produced during the reduction step.

A potential operational problem is the loss of plutonium by volatilization during the reduction step.[23b,c] Calculations based on thermodynamic data have shown[23b] that the plutonium loss may be minimized by conducting the reduction in argon at atmospheric pressure or, if the reaction is carried out under vacuum, by limiting the reaction time to 4 hr and the reaction temperature to 1450°C. It is believed, however, that the loss of plutonium by volatilization is unlikely to be significant in the production of kilogram quantities of (Pu-U)C by direct reduction of the oxides.[23b,c] Results of studies on the volatility of plutonium carbide have been published recently.[23d,24]

Data on the equilibrium phases present in the uranium-plutonium-carbon system were reported by Dalton[23e] and Rosen, Nevitt, and Mitchell.[25] The work of Dalton[23e] concerned the uranium-plutonium-carbon system containing between 50 and 60 at.% carbon at temperatures

up to 2000°C. Rosen, Nevitt, and Mitchell[25] constructed a uranium-plutonium-carbon ternary-phase diagram below 50 at.% carbon.

Preparation of Plutonium Nitride and Plutonium Phosphide

Until recently the prime candidates for fast breeder reactor fuels have been considered to be mixed oxides or carbides of plutonium and uranium. However, advances in the development of UN fuels [see *Reactor Fuel Processing*, 8(1): 55-57, Winter 1964–1965] have led to an interest in PuN as a fissile component in UN-PuN fast breeder reactor fuels. Pardue and associates[26] at Battelle Memorial Institute (BMI) investigated methods for synthesizing PuN and evaluated the product in terms of ease of fabrication and chemical reactivity. Of the several preparation techniques studied, a method based on the direct nitriding of hydrided plutonium metal appeared to be the most satisfactory. The processing procedure involved these steps: (1) plutonium metal was hydrided at 200°C in a hydrogen atmosphere to produce a fine powder of PuH_2, (2) the excess hydrogen was removed by evacuation and the system was heated from 200 to 500°C to decompose the PuH_2, (3) the system was evacuated and then filled with nitrogen, (4) the temperature of the system was raised to 700°C and held at that level for 17 hr, and (5) the nitriding reaction was completed by heating to 1000°C for 1 hr. The product generally contained 5.33 wt.% nitrogen as compared with 5.53 wt.% nitrogen for stoichiometric PuN. The deficiency in nitrogen was attributed to the presence of oxygen contaminant of up to 5000 ppm, which apparently occurred during the hydriding and nitriding steps and not during handling of the product.

Dense PuN specimens were fabricated by an isostatic hot-pressing technique in which consolidated powder sealed in a refractory metal container was subjected to 10,000-psi external gas pressure at 1370 to 1540°C for 3 hr. Attempts to prepare dense PuN bodies by vacuum sintering or sintering under a nitrogen atmosphere were unsuccessful.

Pardue and associates at BMI[27] published the results of an evaluation of plutonium compounds as nuclear fuels. In this study they established a procedure for preparing single-phase plutonium phosphide by the reaction of plutonium powder (prepared by hydriding plutonium sheet followed by thermal decomposition of the hydride) with phosphine gas (PH_3) for 2 hr at 1000°C. The powdered PuP product was densified to greater than 95% of the theoretical density by isostatic hot pressing.

Production and Refining of Plutonium Metal

Plutonium metal is normally produced by the bomb reduction of a plutonium compound by an active metal in a sealed pressure vessel. Inherent in the bomb-reduction process are the need to process a large volume of solid by-product salts for plutonium recovery and the need to provide a new container for each batch of metal produced. Since both these operations are costly, a program to demonstrate the continuous production of plutonium metal by electroreduction from a fused chloride salt has been undertaken at Hanford Atomic Products Operation.[28,29] This process offers the advantage of producing plutonium metal continuously in a manner that requires only occasional replacement of the processing cell and that produces a gaseous by-product which is readily freed of any plutonium content and is easily disposed of.

Nuclear safety is achieved by restricting the system in a 57-mm-diameter envelope (Fig. V-3). This envelope contains the reduction cell and ensures that all forms of plutonium (both in and out of the cell) be contained in a safe geometry. Continuous operation of the reduction cell is achieved by fabricating the cell from a two-piece slip-cast magnesia–10% titania body that forms an annular container with a bottom weir. The molten-plutonium-metal product flows through the weir and is collected in a reservoir beneath the cell (Fig. V-4).

Operating conditions for conducting the electroreduction process are presented in Table V-1. Plutonium trichloride is fed into the apparatus to blend with a melt (at 800°C) to give an electrolyte consisting of 28 wt.% $BaCl_2$, 42 wt.% KCl, and 30 wt.% $PuCl_3$. Application of 30 amp results in the formation of 50 g/hr of plutonium at the cathode. The molten-plutonium product serves as the cathode. The cell has been operated at an average current efficiency

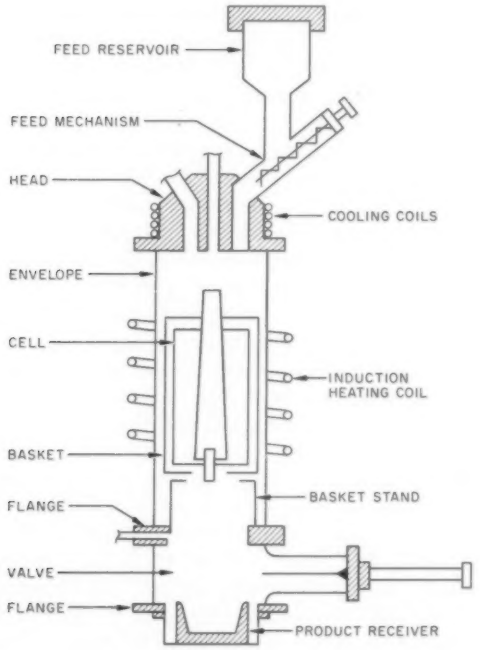

Fig. V-3 Plutonium electrowinning equipment.[29]

of 60%. Hydrogen is introduced at the top of the cell to react with the by-product chlorine formed at the graphite anode and to produce a reducing atmosphere above the cell. Argon is introduced below the cell to protect the metal product from the off-gases.

Runs over 10 hr in duration have been made, and results have indicated that production for longer periods is possible. Best results are obtained when no current interruptions occur and a steady operating state is maintained. Feed is continuously added to the cell from the reservoir, and metal product drips from the bottom weir as it is formed. Prior to shutdown of the cell, the electrolyte is depleted of its plutonium content by shutting off the feed and continuing the direct current until alkali-metal deposition at the cathode commences as indicated by a decrease in the current drawn by the cell. The final plutonium concentration in the electrolyte upon shutdown is usually 2 wt.%. The contents of the cell are removed in the liquid state. Cells usually rupture on cooling since plutonium metal goes through several phase changes on freezing and cooling.

Control of the purity of the plutonium-metal product is governed primarily by the level of impurities present in the feed. A significant reduction in the concentrations of aluminum, chromium, iron, nickel, and titanium, which form volatile chlorides or carbonyls, has been achieved in the electroreduction process. The plutonium product has been shown to pick up significant concentrations of impurities if it contacts nonrefractory materials or if less electropositive metal ions are permitted to reach the cathode area. The electroreduction process has demonstrated the capability of handling plutonium chloride feed materials containing up to 20 wt.% plutonium dioxide.

Fused-salt electrorefining processes have been developed at Los Alamos Scientific Laboratory (LASL) for producing high-purity plutonium metal on the 500-g and 3.5-kg scales.[30–32] This process has been economically applied to the preparation of high-purity metal and to the recycle of impure plutonium-metal scrap. A complete description of the electrorefining equipment and operating procedure was reported in a previous issue of this journal.[33] Recent work[30,31] has concerned the recovery of plutonium from iron and gallium alloys and the separation of plutonium from americium. In electrorefining experiments for the demonstration of the separation of plutonium and gallium on a 3.5-kg scale, the concentration[30] of gallium in plutonium was reduced from 1.0×10^4 to less than 30 ppm. In tests performed with plutonium-iron alloys, the iron concentration[31] was re-

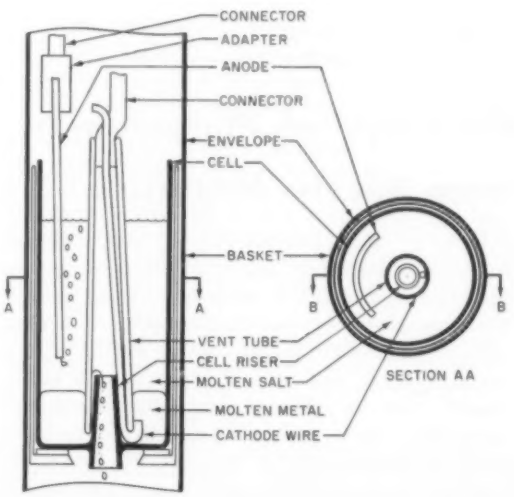

Fig. V-4 Plutonium electrowinning cell.[29]

Table V-1 TYPICAL ELECTROWINNING OPERATING DETAILS[29]

Conditions		
Temperature, °C	800	
Theoretical voltage, volts	2.4	
Voltage across cell, volts	7.6	
Current, amp	30	
Current efficiency, %	60	
Heating, induction, kw	1	
Cell		
Size	$1\frac{1}{2}$ in. in inside diameter by 4 in. high	
Material	Ceramic oxide	
Metal holdup, g	100	
Salt holdup, g	144	
Salt depth, in.	2	
Electrode separation, in.	0.5	
Electrodes		
	Anode	Cathode
Material	Graphite	Molten product
Current density, amp/cm^2	2.0	3.2
Active area, cm^2	15.5	9.4
Feed and product		
	Feed	Product
Material	$PuCl_3$	Plutonium
Melting point, °C	760	640
Density, at 800°C	5.1	16.4
Rate, g/hr	70	50
Salt system		
	Melt	Molten salts
Compositions, wt.%		
$BaCl_2$	40	28
KCl	60	42
$PuCl_3$		30
Melting point, °C	655	580
Density at 800°C	1.9	2.4

duced from 2.5×10^4 to 30 ppm. The separation factor[30] for americium in a $PuCl_3$-NaCl-KCl electrolyte was approximately

$$200 \frac{\text{parts of Am/million parts of Pu (salt phase after run)}}{\text{parts of Am/million parts of Pu (metal product)}}$$

Recovery of Plutonium from Waste Materials

In the production of plutonium compounds and in the preparation of plutonium metal, all waste materials generated in these processing operations must be recycled for plutonium recovery. Waste materials such as casting skulls, reject metal buttons, and lathe turnings may, if sufficiently pure, be recycled simply by melting and recasting. Since impurities, particularly iron, tend to concentrate in the recycle material, much of this material must be purified before reuse. This purification normally involves ignition of the metal to oxide, dissolution of the oxide by refluxing in concentrated nitric acid containing 0.25*M* fluoride, and precipitation as the oxalate, peroxide, or trifluoride. Since this procedure suffers from the low rate of dissolution of plutonium dioxide and the relatively large number of processing steps, Cleveland[34] at Rocky Flats developed a process for the recycle of plutonium-metal scrap based on the dissolution of the metal in a mixture of hydrochloric acid and hydrofluoric acid and the simultaneous precipitation of plutonium as the trifluoride. Since the instantaneous concentration of plutonium in solution is small, the formation of plutonium trifluoride is by homogeneous precipitation, with the result that a precipitate with satisfactory filtration characteristics is obtained without resorting to large solution volumes. After filtration and drying the trifluoride may be reduced with calcium to plutonium metal (using iodine booster) or converted to PuF_4 and reduced to metal (without booster) in yields averaging 98%. (A description of bomb-reduction techniques for plutonium appeared in a previous issue of *Reactor Fuel Processing*.[35]) Plutonium losses to the filtrate are approximately 10 ppm of the metal processed. This recovery process achieves satisfactory purification with respect to iron and carbon but is only partly effective in removing aluminum.

The processing of plutonium generates a wide variety of waste materials that must be processed for plutonium recovery. Wastes, such as polyethylene, paper, rags, wood, and ion-exchange resins, are burned in an incinerator, and the resulting ash containing 1 to 70 wt.% PuO_2 is recovered by dissolution. A dissolution procedure based on the use of 12*N* nitric acid containing 0.4*N* fluoride ion at 100°C has been developed at Rocky Flats.[36] The dissolution rate was observed to increase with temperature and fluoride-ion concentration. Vigorous agitation during dissolution and thorough washing of the undissolved residue were prime requirements for high plutonium recovery.

At the request of the Rocky Flats Division of The Dow Chemical Co., an investigation was made at ANL[37] to determine the feasibility of recovering plutonium from waste materials by the use of fluorine to produce volatile plutonium hexafluoride. This technique is currently being applied to the recovery of uranium and plutonium from spent reactor fuels (see Sec. III of

Table V-2 PLUTONIUM REMOVAL FROM ROCKY FLATS WASTE MATERIALS WITH FLUORINE IN A BOAT REACTION[37]

Waste material*	Sample weight, g	Reaction time, hr	Temp., °C	Fluorine flow, ml/min	Plutonium in residue, g	Plutonium removal, %
Skull oxide	2.0795	9	500†	100†	0.0034	99.8
Skull oxide	4.1120	10	500	200	0.0255	99.3
Skull oxide	3.6811	5	550	200	0.0353	98.9
Incinerator ash	2.2087	5	550	200	0.0455	82.2
Incinerator ash	2.2103	10	550	200	0.0017	99.3
Sweepings	2.151	5	550	200	0.0006	99.9
Sweepings	2.1365	10	550	200	0.0004	99.9
Incinerator ash	2.2677	5	550	200	0.0004	98.8

*On the basis of Rocky Flats analysis, the plutonium content per gram of waste material is as follows: skull oxide, 0.8713 g; incinerator ash, 0.116 g; sweepings, 0.588 g.

†The fluorination procedure for this sample was: 1 hr at 370 to 510°C, F_2 flow rate of 100 ml/min; 4 hr at 510°C, F_2 flow rate of 100 ml/min; 4 hr at 490°C, F_2 flow rate of 500 ml/min.

this issue). Three types of plutonium-bearing waste materials were evaluated: (1) a skull oxide (87.13 wt.% plutonium) that is relatively pure PuO_2, (2) an incinerator ash (11.6 wt.% plutonium), and (3) sweepings (58.8 wt.% plutonium) composed mainly of PuO_2. Samples of these wastes were fluorinated in a horizontal tube furnace with fluorine gas for 5 to 10 hr at 500 to 550°C. The PuF_6 produced was collected in refrigerated traps. The results of these tests are presented in Table V-2. Data reported on plutonium removal from the waste materials are based on determinations of the quantity of plutonium remaining in the residues after fluorination. In general, plutonium removals of 99% or better were achieved. On the basis of these results, it appears that fluorination of plutonium present in these types of waste samples will reduce residual-plutonium concentration to acceptable levels and that this technique might be applied to plutonium-recovery processes by the use of fluid-bed reactors. (J. J. Barghusen)

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